# 5
# Referências Bibliográficas

1. HYNE, N. J. **Nontechnical Guide to Petroleum Geology, Exploration, Drilling, and Production**. 2. ed. Tulsa, Oklahoma: Penn Well Publishing, 1995.
2. TISSOT, B.P.; WELTE, D.H. **Petroleum Formation and Ocurrence**. 2.ed. EUA: Berlin Springer Verlag, 1984.
3. LYONS, W.C.; PLISGA, G.J. **Standard Handbook of Petroleum ε Natural Gas Engineering**. 2. ed. EUA: Elsevier, 2005.
4. The Chemistry of Petroleum Products. Disponível em: http://chemed.chem.purdue.edu/genchem/topicreview/bp/1organic/coal. html #table1_4. Acesso em 16 de agosto de 2007.
5. SYCHRA, V.; LANG, I.; SEBOR, G. Analysis of Petroleum and Petroleum Products by Atomic Absorption Spectroscopy and Related Techniques. **Progress in Analytical Atomic Spectrometry**, v.4, p.341-346, 1981.
6. NELSON, A.J.; REYNOLDS, J.G.; ROOS, J.W. Comprehensive characterization of engine deposits from fuel containing MMT. **Science of the Total Environment**,v.295, p.183-205, 2002.
7. SPEIGHT, J.G. **Handbook of Petroleum Product Analysis**. New Jersey: John Wiley & Sons, 2002.
8. Simanzhenkov, V.; Idem, R. **Crude Oil Chemistry**. New York, EUA: Marcel Dekker, 2003.
9. Características do óleo diesel. Disponível em: http://www.br.com.br/portalbr/calandra.nsf#http://www.br.com.br/portalbr/calandra.nsf/0/7A2FB4F682143AB203256DAD004D0E4F?OpenDocument&SGrandes+Consumidores. Acesso em 19 de setembro de 2007.
10. MATOS REYES, M. N.; CAMPOS, R. C.; VEGUERIA, S. J.; LUNA, A.S. Some studies related to the behaviour of Ni in organic solvents aiming its determination in petroleum fractions by GF AAS. In:

COLLOQUIUM SPECTROSCOPICUM INTERNATIONALE XXXIII: livro de resumos, p 60. 2003, Granada - Espanha.

11. ROBBINS, W.K.; WALKER, H.H. Analysis of petroleum for trace metals – Determination of trace quantities of cadmium in petroleum by atomic absorption spectrometry. **Analytical Chemistry**, v.47, p.2095-2101, 1975.
12. LANG, I.; SEBOR, G.; SYNCHRA, V.; KOLIHOVÁ, D.; WEISSER, O. The determination of metals in petroleum samples by atomic absorption spectrometry. **Analytica Chimica Acta**, v.84, p. 299-305, 1976.
13. MARQUEZ, N.; SAMBERTT, F.Y; DE LA CRUZ, C. Three analytical methods to isolate and characterize vanadium and nickel porphyrins from heavy crude oil. **Analytica Chimica Acta**, v.395, p. 343-349, 1999.
14. BAENA, J.R.; GALLEGO, M.; VALCÁRCEL, M. Speciation of inorganic lead trialkyl-lead compounds by flame atomic absorption spectrometry following continuous selective pre concentration from aqueous solutions. **Spectrochimica Acta Part B**, v.54, p.1869-1879, 1999.
15. BURRAUS, J.A.; HEERDT, J.C.; WILLIS, J.B. Determination of wear metals in used lubricating oils by atomic absorption spectrometry. **Analytical Chemistry**, v.37, p. 579-582, 1965.
16. LUCAS, A.G. **Modern Petroleum Technology**: Downstream. v.2, 6. ed. England: John Wiley & Sons Ed., 2000.
17. LITTLE, D.M. **Catalytic Reforming**. Tulsa: Penn Well Publishing Company, 1985.
18. ELLIOT, W.N.; HEATHEOTE, C.; MOSTYN, R.A. Determinations of phosphurus in lubricating oils by cool-flame emission spectroscopy. **Talanta**, v.19, p. 359-363, 1972.
19. ANTOS, G.J.; AITANI, A.M.; PARRERA J.M. **Catalytic Nafta Reforming**: Science and Technology. New York: Marcel Dekker Ed., 1995.
20. RYABOSSHAPKO, A.; ILIA, I.; GUSEV, A.; AFINOGENOVA, O.; BERG, T.; HJELLBREKKE, A. Monitoring and modelling of lead, cadminum and mercury transboundary transport in the atmosphere of Europe. Methereological Synthesizing Centre Moscow, Russia. Report 1/1999.

21. LIENEMANN, C.P. Analysis of trace metals in petroleum products, state of the art. **Oil & Gas Science and Technology**- Revue del Institut Francais du Petrole, v.60, p.951-965, 2005.
22. FONSECA, T.C.O. **Caracterização inorgânica de petróleos pela técnica de ICP-MS para fins de exploração geoquímica**. Rio de Janeiro, 2000. 135p. Tese (Doutorado em Química) - Departamento de Química, Pontifícia Universidade Católica do Rio de janeiro.
23. KELLY, R.W.; LONG, S.E.; MANN, J.L. Determination of mercury in SRM crude oils and refined products by isotope dilution cold vapor ICP-MS using closed-system combustion. **Analytical and Bioanalytical Chemistry**, v.376, p.753-758, 2003.
24. KOWALEWSKA, Z.; RUSZCZYNSKA, A.; BULSKA, E. Cu determination in crude oil distillation products by atomic absorption and inductively coupled plasma mass spectrometry after analyte transfer to aqueous solution. **Spectrochimica Acta Part B**, v.60, p.351-359, 2005.
25. MONTASER, A. **Inductively Coupled Plasma Mass Spectrometry**, 1.ed. New York: Wiley-VCH, 1998.
26. DUYCK, C.; MIEKELEY, N.; SILVEIRA, C.L.P.; SZATMARI, P. Trace element determination in crude oil and its fractions by inductively coupled plasma mass spectrometry using ultrasonic nebulization of toluene solutions. **Spectrochimica Acta Part B**, v.57, p.1979-1990, 2002.
27. BOTTO, R.I.; ZHU, J. Use of an ultrasonic nebulizer with membrane desolvation for analysis of volatile solvents by inductively coupled plasma atomic emission spectrometry. **Journal of Analytical Atomic Spectrometry**, v.9, p.905-912, 1994.
28. BOTTO, R.I. Applications of ultrasonic nebulization in the analysis of petroleum and petrochemicals by inductively coupled plasma atomic emission spectrometry. **Journal of Analytical Atomic Spectrometry**, v.8, p.51-57, 1993.
29. BOTTO, R.I.; ZHU, J. Universal calibration for analysis of organic solutions by inductively coupled plasma atomic emission spectrometry. **Journal of Analytical Atomic Spectrometry**, v.11, p.675-681, 1996.

30. BOTTO, R.I. Trace element analysis of petroleum naphtas and tars using direct injection ICP-MS. **Canadian Journal of Analytical Sciences and Spectroscopy**, v.47, p.1-13, 2002.

31. BOORN, A.W.; BROWNER, R.F. Effects of organic solvents in inductively coupled plasma atomic emission spectrometry. **Analytical Chemistry**, v.54, p.1402-1410, 1992.

32. BRENNER, I.B.; ZANDER, A.; PLANTZ, M.; ZHU, J.Characterization of an ultrasonic nebulizer-membrane separation interface with inductively coupled plasma mass spectrometry for the determination of trace elements by solvent extraction. **Journal of Analytical Atomic Spectrometry**, v.12, p.273-279, 1997.

33. HUTTON, R.C. Application of inductively coupled plasma source mass spectrometry (ICP-MS) to the determination of trace metals in organics. **Journal of Analytical Atomic Spectrometry**, v.1, p.259-263, 1986.

34. SAINT'PIERRE, T.D.; DIAS, L.F.; POZEBON, D.; AUCÉLIO, R.Q.; CURTIUS, A.J.; WELZ, B. Determination of Cu, Mn, Ni and Sn in gasoline by ETV–ICP-MS and emulsion sample introduction. **Spectrochimica Acta Part B**, v.57, p.1991-2001, 2002.

35. MAGYAR, B.; LIENEMANN, P.; VONMONT, H. Some effects of aerosol drying and oxygen feeding on the analytical performance of an inductively coupled nitrogen–argon plasma. **Spectrochimica Acta Part B**, v.41, p.27-38, 1986.

36. SILVA, I.A. **Estabilização de cobre e chumbo em combustível de aviação utilizando sistemas multi-componentes visando a sua determinação por espectrometria de absorção atômica**. Rio de Janeiro, 1996. 75p. Tese (Doutorado em Química) - Departamento de Química, Pontifícia Universidade Católica do Rio de janeiro.

37. SILVA, I.; CAMPOS, R.C.; CURTIUS, A.J.; SELLA, S.M. Determination of lead and copper in kerosene by electrothermal atomic absorption spectrometry: stabilization of metals in organic media by a three-component solution. **Journal of Analytical Atomic Spectrometry**, v.8, p.749-754, 1993.

38. CAMPOS, R.C.; DOS SANTOS, H.R.; GRINBERG, P. Determination of copper, iron, lead and nickel in gasoline by electrothermal atomic

absorption spectrometry using three-component solution. **Spectrochimica Acta Part B**, v.57, p.15-28, 2002.

39. BRANDÃO, G.P.; CAMPOS, R.C.; LUNA, A.S.; CASTRO, E.V.R.; JESUS, H.C. Determination of arsenic in diesel, gasoline and naphtha by graphite furnace atomic absorption spectrometry using microemulsion medium for sample stabilization. **Analytical and Bioanalytical Chemistry**, v.385, p.1562-1569, 2006.
40. SOUZA, R.M.; MELIANDE, A.L.S.; SILVEIRA, C.L.P. DA; AUCÉLIO, R.Q. Determination of Mo, Zn, Cd, Ti, Ni, V Fe, Mn, Cr and Co in crude oil using inductively coupled plasma optical emission spectrometry and sample introduction as detergentless micro-emulsions. **Microchemical Journal**, v.82, 137-141, 2006.
41. BRUHN, C.; CABALÍN, V. Direct determination of nickel in gas oil by atomic absorption spectrometry with electrothermal atomization. **Analytica Chimica Acta**, v.147, p.193-203, 1983.
42. AUCÉLIO, R.Q.; DOYLE, A.; PIZZORNO, B.S.; TRISTÃO, M.L.B.; CAMPOS, R.C. Electrothermal atomic absorption spectrometric method for the determination of vanadium in diesel and asphaltene prepared as detergentless microemulsions. **Microchemical Journal**, v.78, p. 21- 26, 2004.
43. REYES, M.N.M.; CAMPOS, R.C. Graphite furnace atomic absorption spectrometric determination of Ni and Pd in diesel and gasoline samples stabilized as microemulsion using conventional and permanent modifiers. **Spectrochimica Acta Part B**, v.60, p.615-624, 2005.
44. YEN, T.F. **The Role of Trace Metals in Petroleum**. Michigan: Ann Harbor Science Publishers Inc., 1975.
45. DUYCK, C.B. **Determinação** de **elementos traço em petróleo bruto e suas frações por USN-ICP-MS** de **soluções orgânicas visando aplicações geoquímicas**. Rio de Janeiro, 2001. 203p. Tese (Doutorado em Química) - Departamento de Química, Pontifícia Universidade Católica do Rio de janeiro.
46. MAESSEN, F.J.M.J.; SEEVERENS, P.J.H.; KREUNING, G. Analytical aspects of organic solvent load reduction in normal-power ICPs by aerosol

thermostating at low temperatures. **Spectrochimica Acta Part B**, v.39, p.1171-1180, 1984.

47. HAUSLER, D. Trace element analysis of organic solutions using inductively coupled plasma-mass spectrometry. **Spectrochimica Acta Part B**, v.42, p.63-73, 1987.
48. LOPEZ, L.; LÓ MONACO, S. Geochemical implications of trace elements and sulfur in the saturate, aromatic and resin fractions of crude oil from the Mara and Mara Oeste fields, Venezuela. **Fuel**, v.83, p.365-374, 2004.
49. SNEDDON, J.; HARDAWAY, C.; BOBBADI, K.K.; BECK, J.N. A study of a crude oil spill site for selected metal concentrations remediated by a controlled burning in Southwest Louisiana. **Microchemical Journal**, v.82, p.8-16, 2006.
50. LORD, C.J. Determination of trace metals in crude oil by inductively coupled plasma mass spectrometry with micro-emulsion sample introduction. **Analytical Chemistry**, v.63, p.1594-1599, 1991.
51. WELZ, B.; BECKER-ROSS, H.; FLOREK, S.; HEITMAN, U. **High-resolution Continuum Source AAS**: The Better Way to do Atomic Absorption Spectrometry. 1.ed. Weinheim: Wiley-VCH, 2005.
52. FABEC, J.L.; RUSCHAK, M.L. Determination of nickel, vanadium, and sulfur in crudes and heavy crude fractions by inductively coupled argon plasma/ atomic emission spectrometry and flame atomic absorption spectrometry. **Analytical Chemistry**, v.57, p.1853-1863, 1985.
53. GUIDR, J.M.; SNEDDON, J. Fate of vanadium determined by nitrous oxide– acetylene flame atomic absorption spectrometry in unburned and burned Venezuelan crude oil. **Microchemical Journal**, v.73, p.363-366, 2002.
54. HAMMOND, J.L.; LEE, Y.; NOBLE, C.O.; BECK, J.N.; PROFFITT, C.E.; SNEDDON J. Determination of cadmium, lead, and nickel by simultaneous multielement flame atomic absorption spectrometry in burned and unburned Venezuelan crude oil. **Talanta**, v.47, p.261-266, 1998.
55. CAMPOS, R.C.; RESENDE, M.C.R.; CURTIUS, A.J. Application of the cold vapor technique to the speciation of mercury in fish samples after

solvent extraction and methylmercury reduction directly in the organic medium. **Journal of Analytical Atomic Spectrometry**, v.8, p.247-251, 1993.

56. BRANDÃO, G.P.; CAMPOS, R.C.; LUNA, A.S. Determination of mercury in gasoline by cold vapor atomic absorption spectrometry with direct reduction in micro-emulsion media. **Spectrochimica Acta Part B**, v.60, p.625-631, 2005.
57. ANSELMI, A.; TITTARELLI, P.; KATSKOV, D.A. Determination of trace elements in automotive fuels by filter furnace atomic absorption spectrometry. **Spectrochimica Acta Part B**, v.57, p.403- 411, 2002.
58. KOWALEWSKA, Z.; BULSKA, E.; HULANICKI, A. Organic Palladium-magnesium chemical modifiers in direct determination of lead in fractions from distillation of crude oil by electrothermal atomic absorption analysis. **Spectrochimica Acta Part B**, v.54, p. 835-843, 1999.
59. DAMIN, I.C.F.; VALE, M.G.R.; SILVA, M.M.; WELZ, B.; LEPRI, F.G.; SANTOS, W.N.L.; FERREIRA, S.L.C. Palladium as chemical modifier for the stabilization of volatile nickel and vanadium compounds in crude oil using graphite furnace atomic absorption spectrometry. **Journal of Analytical Atomic Spectrometry**, v.20, p.1332-1336, 2005.
60. VALE, M.G.R.; DAMIN, I.C.F.; KLASSEN, A.; SILVA, M.M.; WELZ, B.; SILVA, A.F.; LEPRI, F.G.; BORGES, D.L.G.; HEITMANN, U. Method development for the determination of nickel in petroleum using line-source and high resolution continuum-source graphite furnace atomic absorption spectrometry. **Microchemical Journal**, v.77, p.131-140, 2004.
61. SILVA, A.F.; WELZ, B.; CURTIUS, A.J. Noble metals as permanent chemical modifiers for the determination of mercury in environmental reference materials using solid sampling graphite furnace atomic absorption spectrometry and calibration against aqueous standards. **Spectrochimica Acta Part B**, v.57, p.2031-2045, 2002.
62. VALE, M.G.R.; SILVA, M.M.; WELZ, B.; NOWKA, R. Control of spectral and non-spectral interferences in the determination of thallium in river and marine sediments using solid sampling electrothermal atomic absorption spectrometry. **Journal of Analytical Atomic Spectrometry**, v.17, p.38-45, 2002.

63. HORNUNG, M.; KRIVAN, V. Determination of silicon in biological tissue by electrothermal atomic absorption spectrometry using slurry sampling of original and pre-ashed samples. **Journal of Analytical Atomic Spectrometry**, v.12, p.1123-1130, 1997.
64. COSKUN, N.; AKMAN, S. Direct determination of phosphorus in different food samples by means of solid sampling electrothermal atomic absorption spectrometry using Pd plus Ca chemical modifier. **Spectrochimica Acta Part B**, v.60, p.415- 419, 2005.
65. VALE, M.G.R.; SILVA, M.M.; WELZ, B.; LIMA, E.C. Determination of cadmium, copper and lead in mineral coal using solid sampling graphite furnace atomic absorption spectrometry. **Spectrochimica Acta Part B**, v.56, p.1859-1873, 2001.
66. SILVA, A.F.; BORGES, D.L.G.; WELZ, B.; VALE, M.G.R.; SILVA, M.M.; KLASSEN, A.; HEITMANN, U. Method development for the determination of thallium in coal using solid sampling graphite furnace atomic absorption spectrometry with continuum source, high-resolution monochromator and CCD array detector. **Spectrochimica Acta Part B**, v.59, p.841- 850, 2004.
67. SILVA, A.F.; BORGES, D.L.G.; LEPRI, F.G.; WELZ, B.; CURTIUS, A.J.; HEITMANN, U. Determination of cadmium in coal using solid sampling graphite furnace high-resolution continuum source atomic absorption spectrometry. **Analytical and Bioanalytical Chemistry**, v.382, p.1835-1841, 2005.
68. RESANO, M.; ARAMENDIA, M.; VOLYNSKY, A.B.; BELARRA, M.A. Solid sampling-graphite furnace atomic absorption spectrometry for the direct determination of trace amounts of silicon in polyamide. Comparison of the performance of platinum and palladium as chemical modifiers. **Spectrochimica Acta Part B**, v.59, p.523-531, 2004.
69. BELARRA, M.A.; CRESPO, C.; MARTINEZ-GARBAYO, M.P.; RESANO, M. Direct determination of cobalt and zinc in samples of different volatility by means of solid sampling-graphite furnace atomic absorption spectrometry. **Spectrochimica Acta Part B**, v.58, p.1847-1858, 2003.

70. REYES, M.N.M.; CAMPOS, R.C. Determination of copper and nickel in vegetable oils by direct sampling graphite furnace atomic absorption spectrometry. **Talanta**, v.70, p.929-932, 2006.
71. AL- SWAIDAN, H.M. Trace Determination of Vanadium and Nickel in Saudi-Arabian Petroleum and Petroleum-Products by Microemulsion ICP-MS. **Atomic Spectroscopy**, v.14, p.170-173, 1993.
72. KUMAR, S.J.; GANGADHARAN, S. Determination of trace elements in naphtha by inductively coupled plasma mass spectrometry using water-in-oil emulsions. **Journal of Analytical Atomic Spectrometry**, v.14, p.967-971, 1999.
73. SOUZA, R.M.; DA SILVEIRA, C.L.P.; AUCÉLIO, R.Q. Determination of refractory elements in used lubricating oil by ICPOES employing emulsified sample introduction and calibration with inorganic standards. **Analytical Sciences**, v.20, p.351-355, 2004.
74. NARASAKI, H. Determination of arsenic and selenium in fat materials and petroleum products by oxygen bomb combustion and automated Atomic-Absorption Spectrometry with hydride generation. **Analytical Chemistry**, v.57, p.2481-2486, 1985.
75. CASSELLA, R.J.; BARBOSA, B.A.R.S.; SANTELLI, R.E.; RANGEL, A.T. Determination of arsenic and antimony in naphtha by Electrothermal Atomic Absorption Spectrometry with microemulsion sample introduction and iridium permanent modifier. **Analytical and Bioanalytical Chemistry**, v.379, p.66-71, 2004.
76. ASTM D 3237-96, Standard Test Method for Lead in Gasoline by Atomic Absorption Spectrometry, 1996.
77. CAPACHO-DELGADO, L.; MANNING, D.C. Determination of vanadium in steels and gas oils. **Atomic Absorption Newsletters**, v.5, p.1- 3, 1966.
78. DE LA GUARDIA, M.; LIZONDO, M.J. Direct determination of nickel in fuel oil by atomic absorption spectrometry using emulsions. **Atomic Spectroscopy**, v.6, p. 208-211, 1988.
79. DU, B.; WEI, Q.; WANG, S.; YU, W. Application of microemulsions in determination of chromium naphthenate in gasoline by Flame Atomic Absorption Spectroscopy. **Talanta**, v.44, p.1803-1806, 1997.

80. BURGUERA, J.L.; DE SALAGER, R.A.; BURGUERA, M.; SALAGER, J.L; RÓNDON, C.; CARRERO, P.; GALLIGNANI, M.; BRUNETTO, M.R.; BRICEÑO, M. On-line emulsification of lubricating oils in a flow-injection system for chromium determination by electrothermal atomic absorption spectrometry. **Journal of Analytical Atomic Spectrometry**, v.15, p. 549-555, 2000.
81. AUCÉLIO, R.Q.; CURTIUS, A. Evaluation of electrothermal atomic absorption spectrometry for trace determination of Sb, As and Se in gasoline and kerosene using microemulsion sample introduction for chemical modification. **Journal of Analytical Atomic Spectrometry**, v.17, p.242-247, 2002.
82. UOP Method 946-96: Arsenic in petroleum naphthas by HG-AAS. 2005. Disponível em: http://www.astm.org.
83. ANEVA, Z.; IANCHEVA, M. Simultaneous extraction and determination of traces of lead and arsenic in petrol by electrothermal atomic-absorption spectrometry. **Analytica Chimica Acta**, v.167, p.371-374, 1985.
84. EPA Method 3031: Acid Digestion of Oils For Metals: Analysis by Atomic Absorption or ICP Spectrometry 1996. Disponível em: http://www.epa.gov/epaoswer/ hazwaste/test/pdfs/3031.pdf.
85. UOP Method 391-91: Trace Metals in Petroleum Products Organics by AAS. 1991. Disponível em: http://www.astm.org.
86. BETTINELLI, M.; SPEZIA, S.; BARONI, U.; BIZZARRI, G. Determination of trace elements in fuel oils by inductively coupled plasma mass spectrometry after acid mineralization of sample in microwave oven. **Journal of Analytical Atomic Spectrometry**, v.10, p.555-560, 1995.
87. BROWN, J.R.; SABA, C.S.; RHINE, W.E.; EISENTRAUT, K.J. Particle size independent spectrometry determination of wear metals in aircraft lubricating oils. **Analytical Chemistry**, v.52, p.2365-2370, 1980.
88. TUELL, T.M.; ULLMAN, A.H.; POLLARD, B.D.; MASSOUMI, A.; BRADSHAW, J.; BOWER, J.N.; WINEFORDNER, J.D. Comparative Study of standards for determination of trace wear metals in jet engine oils. **Analytica Chimica Acta**, v.108, p.351-356, 1979.
89. BELLIDO-MILLA, D.; ORDAZ-GARCIA, S.; GUERRERO-VALIENTE, J.; HERNANDEZ-ARTIGA, M. Rapad Procedure to

determine wear metals in lubricating oils and the análisis of variance in the evaluation of sample preparation procedures. **Mikrochimica Acta**, v.138, p.59-64, 2002.

90. TURUNEN, M.; PERÄNIEMI, S.; AHLGRÉN, M.; WESTERHOLM, H. Determination of trace elements in heavy oil simples by graphite furnace and cold vapour atomic absorption spectrometry after acid digestion. **Analytica Chimica Acta**, v.311, p.85-91, 1995.
91. GONZALEZ M.C.; RODRIGUES A.R.; GONZALEZ V. Determination of vanadium, nickel, iron, copper, and lead in petroleum fractions by atomic absorption spectrophotometry with a graphite furnace. **Microchemical Journal**, v.35, p. 94-106, 1987.
92. KASHIKI, M.; YAMAZOE, S.; OSHIMA, S. Determination of lead in gasoline by atomic absorption spectroscopy. **Analytica Chimica Acta**, v.53, p.95-100, 1971.
93. BYE, R.; PAUS, P.E.; SOLBERG, R.; THOMASSEN, Y. Atomic absorption spectroscopy used as a specific gas chromatography detector: Comparison of flame and graphite furnace techniques in the determinations of tetraalkyllead compounds. **Atomic Absorption Newsletter**, v.17, p.131-134, 1978.
94. HULANICKI, A.; BULSKA, E. Effect of organic solvents on atomization of Ni, Cu and Pb in Graphite Furnace in Atomic Absorption Spectrometry. **Journal of Spectroscopy**, v.29, p.148-152, 1984.
95. MBILENI, C.N.; NGOBENI, P.; KATSKOV, D.A.; PANICHEV, N. Determination of lead and cadmium in organic solutions by electrothermal atomic absorption spectrometry with a transverse heated filter atomizer. **Journal of Analytical Atomic Spectrometry**, v.17, p.236-241, 2002.
96. LUKASIEWICK, R.J.; BUELL, B.E. Study of zinc determination in lubricating oils and additives by atomic absorption spectrometry. **Analytical Chemistry**, v.47, p.1673-1676, 1975.
97. LANG, I.; SEBOR, G.; WEISSER, O.; SYCHRA, V. The determination of the metals in petroleum samples by atomic absorption spectrometry. Part III: The effect of added alkali metals on the determination in vanadium in organic solutions. **Analytical Chimica Acta**, v.88, p.313-318, 1977.

98. TSEROVSKY, E.; ARPADJAN, S. Behaviour of Various Organic Solvents and Analytes in Electrothermal Atomic Absorption Spectrometry. **Journal of Analytical Atomic Spectrometry**, v.6, p. 487-491, 1991.

99. KUMAR, S.J.; GANGADHARAN, S. Determination of trace elements in naphtha by inductively coupled plasma mass spectrometry using water in oil emulsions. **Journal of Analytical Atomic Spectrometry**, v.14, p.967-971, 1999.

100. WEI, Q.; DU, B. Rapid and selective method for the spectrophotometric determination of nickel naphthenate in gasoline in a microemulsion. **Talanta**, v.45, p.957-961, 1998.

101. SHTYKOV, S.N.; MEL'NIKOV, G.V.; SHTYKOVA, L.S. Fluorimetric and conductometric study of water-n-octane-sodium dodecyl sulfate-n-pentanol microemulsions. **Russian Chemical Bulletin**, v.52, p.398-402, 2003.

102. LEE, D.G.; HUTCHISON, J.C.; DESIMONE, J.M.; MURRAY, R.W. Electrochemistry in water-in-supercritical-CO2 microemulsions. **Abstracts of papers of the Chemical Society**, v.222, p.142, 2001.

103. EL-SHERBINY, D.T.M.; EL-ASHRYA, S.M.; MUSTAFA, M.A.; EL-EMAM, A.A.; HANSEN, S.H. Evaluation of the use of microemulsions as eluents in high-performance liquid chromatography. **Journal of Separation Science**, v.26, p.503-509, 2003.

104. NETO, B.B; SCARMINIO, I.S.; BRUNS, R.E. **Como fazer experimentos: pesquisa e desenvolvimento na ciência e na indústria**. Campinas, São Paulo: Editora da Unicamp, 2001.

105. MILLER, J.C.; MILLER, J.N. **Statistics for analytical chemistry**. 3.ed. New York: Ellis Horwood PTR Prentice Hall, 1993.

106. ASTM Method D 3831-90: Standard Test Method for manganese in gasoline by Atomic Absorption Spectroscopy. 1990.

107. ASTM Method 5863-B: International Standard Test Methods for Determination of Nickel, Vanadium, Iron, and Sodium in Crude Oils and Residual Fuels by Flame Atomic Absorption Spectrometry. Reapproved 2005.

108. GONZÁLEZ, M.C.; RODRIGUEZ, A.R.; GONZÁLEZ, V. Determination of vanadium, nickel, iron, copper, and lead in petroleum

fractions by atomic absorption spectrophotometry with a graphite furnace. **Microchemical Journal**. v.35, p.94-106, 1987.

109. GRINBERG, P.; CAMPOS, R.C. Iridium as permanent modifier in the determination of lead in whole blood and urine by electrothermal atomic absorption spectrometry, **Spectrochimica Acta Part B**, v.56, p.1831-1843, 2001.

110. LEPRI, F.G.; WELZ, B.; BORGES, D.L.G.; SILVA, A.F.; VALE, M.G.R.; HEITMANN U. Speciation analysis of volatile and non-volatile vanadium compounds in Brazilian crude oils using high-resolution continuum source graphite furnace atomic absorption spectrometry, **Analytical Chimica Acta**, v.558, p.195-200, 2006.

111. SILVA, M.M.; DAMIN, I.C.F.; VALE, M.G.R.; WELZ, B. Feasibility of using solid sampling graphite furnace atomic absorption spectrometry for speciation analysis of volatile and non-volatile compounds of nickel and vanadium in crude oil. **Talanta**, v.71, p.349-359, 2007.

112. Loos-Vollebregt, M.T.C.; Galan, L. Zeeman Atomic Absorption Spectrometry, **Progress in Analytical Atomic Spectroscopy**, v.8, p.47-81, 1985.

113. Gleisner, H.; Eichardt, K.; Welz, B. Optimization of analytical performance of a graphite furnace atomic absorption spectrometer with Zeeman-effect background correction using variable magnetic field strength. **Spectrochimica Acta B**, v.58, p.1663-1678, 2003.

114. BRANDÃO, G.P.; CAMPOS, R.C.; DE CASTRO, E.V.R.; DE JESUS, H.C. Direct determination of nickel in petroleum by solid sampling-graphite furnace atomic absorption spectrometry. **Analytical and Bioanalytical Chemistry**, v.386, p.2249-2253, 2006.

115. STIGTER, J.B.; DE HAAN, H.P.M., GUICHERIT, R.; DEKKERS, C.P.A.; DAANE, M.L. Determination of cadmium, zinc, copper, chromium and arsenic in crude oil cargoes. **Environmental Pollution**, v.107, p. 451-464, 2000.

ELSEVIER

Spectrochimica Acta Part B 62 (2007) 962–969

SPECTROCHIMICA ACTA PART B

www.elsevier.com/locate/sab

# Determination of copper, iron and vanadium in petroleum by direct sampling electrothermal atomic absorption spectrometry ☆

Geisamanda Pedrini Brandão [a,*], Reinaldo Calixto de Campos [a], Eustáquio Vinicius Ribeiro de Castro [b], Honério Coutinho de Jesus [b]

[a] *Department of Chemistry, Pontifical Catholic University, Rua Marquês de S. Vicente, 225, Gávea, 22453-900, Rio de Janeiro, RJ, Brazil*
[b] *Department of Chemistry, Espírito Santo Federal University, Avenida Fernando Ferrari, s.n, Campus de Goiabeiras, 29000-000, Vitória, ES, Brazil*

Received 6 December 2006; accepted 1 May 2007
Available online 10 May 2007

## Abstract

A procedure for the direct determination of Cu, Fe and V in petroleum samples by electrothermal atomic absorption spectrometry using a solid sampling accessory, without any sample pre-treatment or dilution, is proposed. A Pd+Triton X-100 solution was used as chemical modifier. The pyrolysis and atomization temperatures, as well as the Pd mass were defined by multivariate optimization. The other parameters of the temperature programs were defined by univariate optimization. The limits of detection at the optimized conditions were 10, 200 and 800 pg for Cu, Fe and V, respectively, for typical sample masses ranging from 0.10 to 3.00 mg. Method accuracy was confirmed by the analysis of oil certified reference materials as well as by comparison with independent methods. Aqueous calibration solutions were used and no statistically significant difference (analysis of variance) was observed between obtained and expected values.

*Keywords:* Copper; Iron; Vanadium; Petroleum; Direct samplimg; ET AAS

## 1. Introduction

Petroleum is a complex mixture of hydrocarbons (between 50 and 95% by weight) and non-hydrocarbons (mainly sulphur, nitrogen, oxygen and heavy metal compounds). Vanadium, nickel, iron and copper are normally found in petroleum as naturally occurring elements associated to the formation process [1–4], and although present only in small amounts ($\mu g\ g^{-1}$ or $ng\ g^{-1}$ levels), they are very important to the petroleum industry [5]. Their determination is of considerable importance, since they have deleterious effects on refinery operation and performance: They may corrode refinery equipment, poison and foul catalysts and/or cause undesirable side reactions in refinery operations [4,6–10]. Also, metallic traces in petroleum are of interest due to their potential of contaminating the environment [8,11]. Altogether, the availability of rapid, accurate, and precise methods for metal determination in petroleum and their products, both at trace levels and at minor concentration, is essential [12].

Several analytical methods for Fe, Cu and V determination in petroleum and its viscous heavy products have been proposed: Inductively coupled plasma optical emission spectrometry (ICP OES) [6,13,14], inductively coupled plasma mass spectrometry (ICP-MS) [9,15–19], flame atomic absorption spectrometry (F AAS) [6,20–22], electrothermal atomic absorption spectrometry (ET AAS) [10,23–27], high performance liquid chromatographic (HPLC) for speciation studies [8,28] and X-ray fluorescence spectroscopy [29]. ICP techniques are well suited for this determination. However, when dealing with highly organic loaded liquids the usual sample introduction nebulization systems lead to problems such as plasma extinction and carbon deposition on the sampler and skimmer cones. To minimize these problems, strategies such as desolvatation under cryogenic cooling using a direct injection nebulizer (DIN) and the removal of carbon by feeding oxygen into the plasma have been proposed [18], as well as sequential injection [17] and ultrasonic nebulization [9]. In contrast, F AAS makes possible the direct analysis of the

---

☆ This paper was presented at the 9th Rio Symposium on Atomic Spectrometry, held in Barquisimeto, Venezuela, 5–10 November 2006, and is published in the special issue of Spectrochimica Acta Part B, dedicated to that conference.

* Corresponding author. Fax: +55 21 3527 1309.
*E-mail address:* rccampos@rdc.puc-rio.br (G.P. Brandão).

0584-8547/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.sab.2007.05.001

hydrocarbon matrix after just a dilution with an adequate organic solvent. However, the solvent and the compounds used for calibration may have a strong influence on the sensitivity causing accuracy problems [30,31]. Also, this technique presents low sensitivity for many applications. ET AAS is a valuable alternative: It presents adequate sensitivity and allows the elimination of the majority of the matrix during the heating program, minimizing the interference problems relative to the matrix characteristics.

In general, all these techniques require a sample pre-treatment previous to the instrumental determination of metals in petroleum and their products. Sample pre-treatment may involve mineralization [8,13,19,20,28,31], extraction [3,8,19], chromatographic separation [8,9], dilution [6,9,10,18,25,26,32], emulsion [13,17,23,24,27] or microemulsion [14–16] formation. Mineralization, extraction and chromatographic separation are time-consuming and suffer from increased risks of contamination and losses, although the final aqueous solution obtained is simpler to deal with and calibration offers no problems. Dilution procedures are simple and proved to be efficient. However, they deteriorate the overall limit of detection of the method due to the usually high dilution factor needed, and the use of organic solvents is harmful to the health of the lab personnel and to the environment. Emulsion formation is also attractive, but the short term physical stability usually associated to emulsions impairs the full use of the autosampler devices. On the other hand, microemulsions are spontaneously formed and stable over extended periods of time.

Direct sampling is an attractive strategy for trace determination: It requires no sample pre-treatment, avoiding the risks of contamination and losses associated to this step, and the full instrumental detection capability can be reached. The main disadvantages related to direct sampling are associated to the sample homogeneity, due to the low sample mass usually introduced, calibration difficulties and matrix effects, since the bulk matrix is presented to the equipment. However, the elimination of a substantial part of the matrix during the pyrolysis stage, the strict obedience to the STPF rules, as well as the use of modern instrumentation have made ET AAS especially well fitted for direct sampling. Nevertheless, in the analysis of complex organic samples the removal of most matrix during the pyrolysis stage generally requires temperatures above 600 °C and metal losses in petroleum and its derivates have been observed at temperatures as low as 400 °C if no chemical modifier is used [12,23,24,27,33]. Therefore the study of chemical modification is mandatory for this application. Aqueous calibration has proved possible, signifying the absence of spectral or non-spectral interferences. Also, the use of alternate lines or field intensities (in Zeeman-effect background corrected equipment with this possibility) extends the dynamic range of the analysis in a situation where sample dilution is not an alternative. The advantages of direct sampling ET AAS, usually associated with solid samples, has been proved to be extensive to viscous liquid samples, such as petroleum [12] and vegetable oils [34]. In these cases, since the samples are easier to homogenize, limitations associated to the sample homogeneity are also minimized. Thus, the present work proposes a procedure for the direct determination of Cu, Fe and V in petroleum samples by direct sampling ET AAS, using a solid sampling accessory, avoiding any sample pre-treatment.

## 2. Experimental

### 2.1. Instrumentation

The Cu, Fe and V ET AAS measurements were performed with a model ZEEnit 60 atomic absorption spectrometer (Analytik Jena, Jena, Germany), equipped with a transversally heated graphite atomizer and a transverse Zeeman-effect background correction system. The samples were weighed onto graphite platforms (Analytik Jena Part No. 407-152.023) especially designed for solid sampling, and inserted into solid sampling tubes without dosing hole (Analytik Jena Part No. 07-8130325). The sample platform was inserted using a SSA 6Z solid sampling accessory (Analytik Jena, Germany). Hollow cathode lamps (Analytik Jena) for Cu, Fe and V, operated at 2, 6 and 12 mA, respectively, were used as line sources. The spectral band pass was fixed at 0.2 nm and the lines used were 324.8 nm for Cu, 248.3 and 302.1 nm for Fe, and 318.4 and 306.1 nm for V. The magnetic field was operated using the 2-field mode at 0.8, 0.8 and 0.4 Tesla for Cu, Fe and V, respectively. A model AD-4 (Perkin Elmer, Norwalk, CT, USA) analytical micro-balance was used for sample weighing. All measurements were made in integrated absorbance, with a 10s integration time. For the Cu and Fe comparative procedures, the GF AAS measurements were performed with a model AAS 5 EA atomic absorption spectrometer (Carl Zeiss, Germany) with a continuum source (deuterium lamp) background corrector and an AS-42 autosampler; graphite tubes with platform were used (Analytik Jena Part No. 407.A81.026); hollow cathode lamps (Analytik Jena) operated at 3 and 5 mA for Cu and Fe, respectively were used as line sources; the spectral band pass was fixed at 0.8 and 0.2 nm and the measurements were performed at 324.8 and 344.1 nm for Cu and Fe, respectively, in the integrated absorbance mode. For the V comparative procedure, the measurements were performed by F AAS, using a model 1100B atomic absorption spectrometer (Perkin Elmer, Norwalk, CT, USA) with a continuum source (deuterium lamp) background corrector; an Analytik Jena V hollow cathode lamp, operated at 15 mA was used as line source ($\lambda = 318.4$ nm); the spectral band pass was 0.7 nm and all measurements were made in peak height within a 15 s observation window.

### 2.2. Materials, reagents, solutions and samples

Argon (99.99%, AGA, Rio de Janeiro, Brazil) was used as protective and carrier gas. Ultrapure water, obtained from a Gehaka Master System apparatus (Gehaka, São Paulo, Brazil) was used throughout. Analytical grade $HNO_3$ (Vetec, Rio de Janeiro, Brazil) was purified by distillation using an of Teflon$^R$ subboiling still (Kürner Analysentechnik, Rosenheim, Germany). The 1000 μg mL$^{-1}$ stock solutions of Cu, Fe and V were prepared by adequate dilution of Titrisol concentrates (Merck, Darmstadt, Germany) with 0.2% v/v $HNO_3$. Aqueous calibration solutions were prepared by further dilution of the stock solutions with 0.2% v/v $HNO_3$. Organometallic stock solutions (Cu, 5000 μg g$^{-1}$; Fe, 5000 μg g$^{-1}$ and V, 100 μg g$^{-1}$) in oil (Conostan, Houston, USA) were also used. The organometallic calibration solutions were

Table 1
Preliminary experiments for the determination of Cu, Fe and V in a petroleum sample by ET AAS (mean and standard deviation; $n=3$) without a modifier and using different chemical modifiers; 'expected concentrations' were obtained by ICP OES after mineralization

| Element | Modifier | | | | Expected value |
|---|---|---|---|---|---|
| | None | Ir permanent | Pd | | |
| | | | Added before the sample | Added after the sample | |
| Cu, ng $g^{-1}$ | 82 ± 13 | 51 ± 8 | 90 ± 10 | 102 ± 9 | 110 ± 9 |
| Fe, µg $g^{-1}$ | 8.5 ± 1.5 | 3.2 ± 0.9 | 7.1 ± 1.2 | 8.2 ± 0.4 | 9.4 ± 0.9 |
| V, µg $g^{-1}$ | 21.7 ± 0.7 | 17.6 ± 1.9 | 24.8 ± 2.5 | 27.6 ± 1.6 | 32 ± 4 |

prepared by adequate dilution of these stock solutions with base-oil 75 (Spex, Metuchen, USA). The conventional modifier solution was prepared from a 10,000 µg mL$^{-1}$ $Pd(NO_3)_2$ stock solution (Merck, Darmstadt, Germany). It consisted of a 1500 µg mL$^{-1}$ Pd solution in 0.1% v/v $HNO_3$ and 0.025% v/v Triton X-100 (Vetec, Rio de Janeiro, Brazil). The permanent modifier was prepared from a 5000 µg mL$^{-1}$ $IrCl_3$ stock solution in 10% v/v $HNO_3$ (Fluka, Buchs, Switzerland). For the comparative procedures xylene (Vetec, Rio de Janeiro, Brazil) and a 1000 µg g$^{-1}$ organic aluminum stock solution in oil (Conostan, Houston, USA) were used. All plastic and glassware was washed with tap water, immersed in Extran (48 h), rinsed with tap and deionized water, and immersed in 20% v/v $HNO_3$ for at least 24 h. Before use these materials were thoroughly rinsed with ultrapure water and oven dried at 40 °C, avoiding any contact with metallic surfaces and dust contamination. Contamination was always checked by a strict blank control. The petroleum samples were obtained from Petrobras. NIST 1634c (Trace Elements in Fuel Oil) and NIST 1085a (Wear-Metals in Oil) certified reference materials were used in the accuracy tests. According to their certificates minimum sample masses of 1 and 0.5 g, respectively, should be used to assure that the results are representative, and the fuel oil material must be warmed before sampling. ASTM CO 0403, 0311 and 0504 crude oil reference materials were also used for the accuracy tests. All results are the average of, at least, 3 replicates.

### 2.3. Procedures

#### 2.3.1. Proposed procedure

The petroleum samples were manually shaken for homogenization. No sample warming was necessary, since the samples were fluidic enough for a good homogenization at room temperature. A sample aliquot (0.10 to 3.00 mg for Cu and Fe or 0.10 to 1.50 mg for V) was transferred to the sample platform and weighed at the micro-balance. The sample transfer to the sample platform was performed with the help of a disposable pipette tip which was first inserted into the sample, and in sequence, gently touched the sample platform surface. Twenty microliters of the Pd modifier solution were then manually deposited onto the sample platform, over the sample. The sample platform was inserted into the graphite furnace using the solid sampling accessory. Calibration was performed in a similar way by weighing increasing masses of the aqueous calibration solutions (Cu, 200 ng mL$^{-1}$; Fe, 10 µg mL$^{-1}$; V, 50 µg mL$^{-1}$ all in 0.2% v/v $HNO_3$).

#### 2.3.2. Copper and iron comparative procedure [10]

A petroleum sample aliquot (1.0 g weighed to the nearest 0.0001 g) was diluted to 5.00 (Cu) or 10.00 mL (Fe) with xylene. Twenty microliters of this solution were analyzed by ET AAS, at 324.8 nm and 344.1 nm for Cu and Fe, respectively, using continuum source (deuterium lamp) background correction.

#### 2.3.3. Vanadium comparative procedure [22]

To 1.0 g of the petroleum sample (weighed to the nearest 0.0001 g), about 0.075 g of a 1000 µg g$^{-1}$ organic Al stock solution in oil was added. This mixture was diluted to 5.0 mL with xylene and analyzed by F AAS at 318.4 nm, using a nitrous oxide/acetylene flame and continuum source (deuterium lamp) background correction.

## 3. Results and discussion

### 3.1. Preliminary tests

#### 3.1.1. Chemical modifiers

The need for, and the performance of conventional (Pd) and permanent (Ir) modifiers were investigated using both aqueous calibration solutions and a petroleum sample. In this experiment, the resonance lines and the 2-field mode at 0.80 Tesla were used. The furnace temperature program and the Pd modifier mass (30 µg) were similar to those used in a previous work for the determination of Ni in petroleum [12]. The Pd modifier was added by dispensing 20 µL of the Pd + Triton X-100 solution either onto the sample platform before the sample (or calibration solution) or after the sample had been deposited. If dispensed before the sample, the modifier solution was dried at 100 °C before the sample/calibration solution was added. The presence of Triton X-100 in the Pd modifier solution came from a previous study [12]

Table 2
Studied factors and their respective levels for Cu, Fe and V by central composite design

| | Level | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Cu | | | | | Fe | | | | | V | | | | |
| Factor | −1.68 | −1 | 0 | +1 | +1.68 | −1.68 | −1 | 0 | +1 | +1.68 | −1.68 | −1 | 0 | +1 | +1.68 |
| Pyrolysis temperature, °C | 625 | 720 | 860 | 1000 | 1095 | 748 | 850 | 1000 | 1150 | 1252 | 764 | 900 | 1100 | 1300 | 1436 |
| Atomization temperature, °C | 2250 | 2270 | 2300 | 2430 | 2518 | 2432 | 2500 | 2600 | 2700 | 2768 | 2432 | 2500 | 2600 | 2700 | 2768 |
| Pd mass, µg | 3 | 10 | 20 | 30 | 37 | 3 | 10 | 20 | 30 | 37 | 3 | 10 | 20 | 30 | 37 |

where erratic results were avoided this way. In the investigation of the Ir permanent modifier, 20 µL of the 5000 µg $mL^{-1}$ Ir solution was dispensed onto the sample platform, and the coating temperature program described by Grinberg et al. [35] was followed. This procedure was repeated 6 times, resulting in a total of 600 µg of Ir on the sample platform. Aqueous calibration solutions (in 0.2% v/v $HNO_3$) were used throughout. The results of this preliminary study are shown in Table 1. For comparison, results obtained by ICP OES after microwave-assisted acid mineralization are also displayed, and taken as expected values. The results in Table 1 indicate that the permanent modifier, at least under the present conditions, is not efficient and further investigation is necessary if it is to be used for the direct ET AAS analysis of petroleum. The best results with the conventional modifier were observed by dispensing the modifier over the sample: In this way, no significant difference was observed between found and expected results; In the case of Fe this was also true when no modifier was used. However, an F-test showed that the repeatability is significantly better when the modifier (dispensed over the sample) is used. The need for a chemical modifier in this kind of analysis is in concordance with other findings in the literature that report Ni and V losses from petroleum samples at low pyrolysis temperatures if no modifier is used [12,24,27]. Thus, the conventional Pd+Triton X-100 modifier, deposited over the sample, was used in further investigations.

### 3.1.2. Analytical line and magnetic field

The aim of the present work was the direct determination of the studied elements in petroleum, avoiding any sample pretreatment, including dilution. However, Fe and V are normally present in petroleum at high concentration (µg $g^{-1}$ level). Thus, the two instrumental ways available for lowering the sensitivity were investigated: The use of alternate lines and varying the magnetic field strength used for Zeeman-effect background correction (maximum sensitivity with the 2-field mode and 0.80 Tesla). The influence of the magnetic field strength on the AAS measurement sensitivity is discussed elsewhere [36,37]. The study was carried out with a petroleum sample and took into account both the sensitivity and the signal-to-background ratio. For Fe determination, the 302.1-nm secondary line was chosen and it was not necessary to reduce the magnetic field strength, which was kept at 0.80 Tesla. Under these conditions, all the investigated petroleum samples fell within the linear range of the analytical curve. However, if petroleum samples with higher Fe concentrations are to be analyzed, the sensitivity can be reduced by 30% using a magnetic field strength of 0.40 Tesla. For V, the 306.1-nm secondary line was chosen and a field strength of 0.40 Tesla, which resulted in a 30% sensitivity drop. At 0.60 Tesla the observed sensitivity drop was only about 5% while at 0.20 Tesla this drop was 70%. These values equally hold for Fe and V, however, the 0.20 Tesla field could not be used, since accurate background correction was not possible in such a low field. For the determination of Cu, due to the low concentration generally found in petroleum (ng $g^{-1}$ level), decreasing the sensitivity was not necessary and the instrumental conditions were those of highest sensitivity, that is $\lambda$=324.8 nm and 2-field mode at 0.80Tesla.

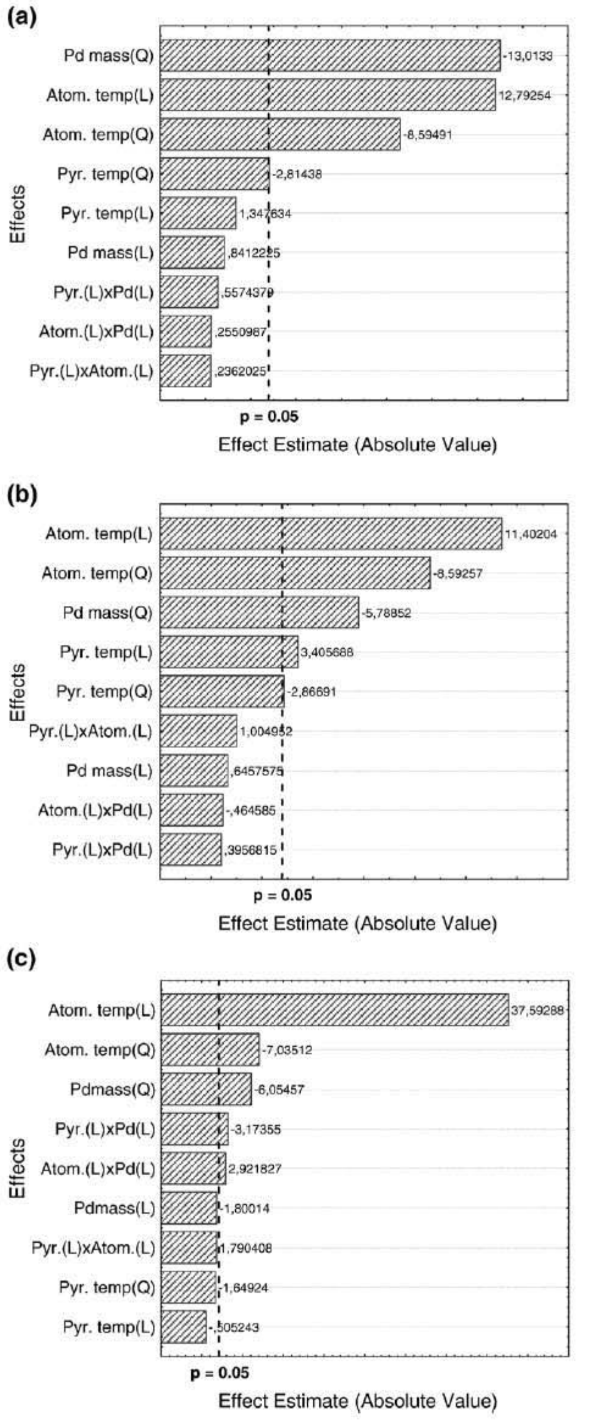


Fig. 1. Pareto charts of standardized effects for (a) Cu, (b) Fe and (c) V from the central composite design. (L) = linear and (Q) = quadratic behavior.

### 3.2. Optimization of the proposed procedure

The drying temperature and ramp, atomization ramp, cleanout temperature and Pd solution volume, were defined

Table 3
Regression coefficients and critical (optimum) values of the studied factors for Cu, Fe and V derived from the central composite design

| | Regression coefficients [a] | | | | | | | | | | Critical (optimum) values [b] | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Intercept | $Tp^2$ | $Ta^2$ | $m^2$ | Tp | Ta | m | Tp.Ta | Tp.m | Ta.m | Tp (°C) | | Ta (°C) | | m (μg) | |
| | | | | | | | | | | | Real | Cod | Real | Cod | Real | Cod |
| Cu | 22,50180 | −0.28549 | −0.87187 | −1.32007 | ns | 1.29594 | ns | ns | ns | ns | 901 | 0.29 | 2398 | 0.75 | 20.5 | 0.05 |
| Fe | 1.463297 | −0.02286 | −0.068521 | −0.046160 | 0.027122 | 0.090802 | ns | ns | ns | ns | 1114 | 0.76 | 2665 | 0.72 | 20.5 | 0.05 |
| V | 13.95739 | ns | −1.28974 | −1.10998 | ns | 5.67188 | ns | ns | −0.62532 | 0.57572 | 1312 | 1.06 | 2839 | 2.39 | 22 | 0.20 |

[a] Intercept, Tp, Ta, m and ns refer to intercept, pyrolysis temperature, atomization temperature, modifier mass, and "non significant", respectively.
[b] Cod refers to codified.

by univariate optimization. A slow drying ramp (2 °C $min^{-1}$) was necessary as well as a high drying temperature (350 °C) in order to avoid sample projection in the pyrolysis stage. The lowest cleanout temperatures that avoided memory effects were chosen (2600, 2700 and 2750 °C for Cu, Fe and V, respectively). The Pd modifier solution volume (20 μL) was that necessary to fully cover the petroleum sample in the sample platform, without overflow.

Multivariate optimization was used for determining the best pyrolysis and atomization temperatures as well as the Pd mass [38]. A petroleum sample was used. In principle, a complete factorial design ($2^3$) was followed, with 3 factors and 2 levels. The $2^3$ (8) experiments were made at a random order. The data were analyzed by using the Statistica 6.0 Statsoft software and the $2^{(k-p)}$ standard design [39]. In this optimization step, all the factors and some interactions have shown statistic significance ($p<0.05$) for all elements studied. However, the F-test showed lack of fit for all elements indicating that the proposed linear model was not adequate. Thus, the factors were optimized by a central composite design. This design makes use of central points that are expanded with a group of 'star points' allowing the estimation of the curvature. The distances from the central to the closest points are taken as ±1, and the distance from the central to a 'star' point is $\pm\alpha$, with $\alpha=\pm(2^{\text{factors number}})^{1/4}$, for keeping rotatability (all 'star' points with the same distance to the central point). In our case, there were 8 ($2^3$) experiments related to the factorial design, 6 ($2\times3$) star experiments ($\alpha=\pm8^{1/4}$) and 2 central experiments. The central points were chosen taking into account the previous factorial design results and other work [12,24,25]. The 16 experiments were randomly performed with a petroleum sample, and the different levels for each element are shown in Table 2. The 16 data ($n=3$) were analyzed using the Statistica 6.0 software (central composite, non-factorial, surface designs) [39]. The Pareto diagrams in Fig. 1 show the significant effects ($p<0.05$) for each element. The $R^2$ adjusted value for Cu was 0.925, or, 92.5% of the variation around the average could be explained by the model. For Fe and V the $R^2$ adjusted values were 0.866 and 0.969, respectively. Other statistical techniques, such as the analysis of normal probability plots as well as the desirability functions have shown similar results, confirming the correctness of the model. The critical points, as well the regression coefficients are shown in Table 3. For V, the critical atomization temperature was above the studied range and also above of the maximum temperature recommended for the instrument. Therefore, a 2700 °C atomization temperature was chosen, the highest to be used in routine work. All other critical points were within the studied ranges, confirming their adequacy. Table 4 summarizes the optimized furnace temperature programs. Under these conditions well resolved peak shapes were observed and the background attenuation was always within the correction capacity of the equipment.

### 3.3. Calibration

Calibration curves established with aqueous standards (0.2% $HNO_3$ v/v) were compared with those established with organometallic solutions (Conostan standards diluted in base oil

Table 4
Optimized temperature program for the determination of Cu, Fe and V in petroleum samples by direct sampling ET AAS (a)

| Step | Operation | Cu | | | | Fe | | | | V | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Temp. | Ramp | Hold | Gas Flow(b) | Temp. | Ramp | Hold | Gas Flow(b) | Temp. | Ramp | Hold | Gas flow(b) |
| | | °C | °C $s^{-1}$ | s | | °C | °C $s^{-1}$ | s | | °C | °C $s^{-1}$ | s | |
| 1 | Drying | 90 | 10 | 5 | Max. | 90 | 10 | 5 | Max. | 90 | 10 | 5 | Max. |
| 2 | Drying | 150 | 10 | 5 | Max. | 150 | 10 | 5 | Max. | 150 | 10 | 5 | Max. |
| 3 | Drying | 350 | 2 | 10 | Max. | 350 | 2 | 10 | Max. | 350 | 2 | 10 | Max. |
| 4 | Pyrolysis | 900 | 50 | 20 | Max. | 1100 | 50 | 10 | Max. | 1300 | 50 | 20 | Max. |
| 5 | Auto-zero | 900 | 0 | 6 | Stop | 1100 | 0 | 6 | Stop | 1300 | 0 | 6 | Stop |
| 6 | Atomize | 2400 | 2400 | 9 | Stop | 2650 | 2500 | 10 | Stop | 2700 | 1800 | 10 | Stop |
| 7 | Cleanout | 2600 | 1000 | 3 | Max. | 2700 | 500 | 2 | Max. | 2750 | 100 | 2 | Max. |

a) 20 μL of 1000 μg $mL^{-1}$ Pd (in 0.025% Triton X-100) as chemical modifier.
b) Max = 2 L $h^{-1}$.

Table 5
Determination of Cu, Fe and V by the proposed and comparative procedures in certified reference materials and petroleum samples (A to N)

| Sample | Cu, ng $g^{-1}$* | | | Fe, µg $g^{-1}$* | | | V, µg $g^{-1}$* | | |
|---|---|---|---|---|---|---|---|---|---|
| | Reference value | Proposed procedure | Comparative procedure [10] | Reference value | Proposed procedure | Comparative procedure [10] | Reference value | Proposed procedure | Comparative procedure [22] |
| ASTM CO 0311 | – | 149±18 | 150±7 | 7±2 | 9±1 | 12±2 | 32±5 | 32±2 | 34±4 |
| ASTM CO 0403 | – | 85±8 | 110±6 | 1.8±0.3 | 1.7±0.4 | 1.9±0.1 | 24±4 | 24.8±0.8 | 26±2 |
| ASTM CO 0504 | – | 44±4 | 45±2 | 1.5±0.7 | 0.6±0.2 | 0.4±0.1 | 257±35 | 252±12 | 230±14 |
| NIST 1634c | 690±60▲ | 685±35 | 746±53 | – | 92±1 | 73±23 | 28.2±0.4 | 28±3 | 24±4 |
| NIST 1085a | – | – | – | 100±2 | 107±6 | 100±2 | – | – | – |
| A | – | <4 | <9 | – | 1.04±0.04 | 1.0±0.2 | – | 18±2 | 19±2 |
| B | – | 9.1±0.7 | <9 | – | 2.5±0.1 | 2.1±0.1 | – | 31±3 | 29±3 |
| C | – | 8±2 | <9 | – | 1.6±0.3 | 1.0±0.1 | – | 23.5±0.4 | 23±3 |
| D | – | 6±2 | <9 | – | 3.2±0.3 | 2.7±0.1 | – | 40±3 | 34±6 |
| E | – | <4 | <9 | – | 1.1±0.1 | 1.1±0.1 | – | 27±1 | 23±3 |
| F | – | <4 | <9 | – | 0.8±0.1 | 0.9±0.1 | – | 22.3±0.9 | 20±2 |
| G | – | <4 | <9 | – | 0.90±0.04 | 0.9±0.1 | – | 23.3±0.2 | 19.4±3.3 |
| H | – | 21±5 | 22±1 | – | 5.9±0.3 | 6.2±0.4 | – | 5.4±0.2 | 3.9±0.9 |
| I | – | <4 | <9 | – | 3±1 | 1.5±0.1 | – | 2.3±0.1 | 1.8±0.4 |
| J | – | 20.5±0.6 | 17±2 | – | 12±1 | 8.9±0.3 | – | 3.8±0.3 | 1.8±0.5 |
| K | – | 267±2 | 368±27 | – | 19.1±0.1 | 19±3 | – | 5.0±0.5 | 3.6±0.9 |
| L | – | 9.3±0.1 | 10±3 | – | 9.4±0.5 | 6.4±0.1 | – | 22.1±0.8 | 17.7±4.0 |
| M | – | <4 | <9 | – | 12.1±0.9 | 8.5±0.1 | – | 25±1 | 19±4 |
| N | – | 24±6 | 22±2 | – | 3.1±0.1 | 2.7±0.1 | – | 5.9±0.1 | 5±1 |

*± standard deviation, $n=3$; – not determined; ▲ determined by ICP OES after microwave-assisted acid mineralization.

75), using the optimized furnace temperature programs and Pd as modifier. The solutions were dispensed onto the sample platform and submitted to the same procedure as described for the samples (Section 2.3.1). For all elements, good linearity was observed with both types of calibration solutions and no significant difference (Student $t$-test, $p<0.05$) between their respective slopes was observed (Cu: $y=0.949$ ($\pm 0.002$)$x$ and $R^2=0.9988$ (aqueous) versus $y=0.952$ ($\pm 0.002$)$x$ and $R^2=0.9974$ (organic); Fe: $y=0.231$ ($\pm 0.002$)$x$ and $R^2=0.9978$ (aqueous) versus $y=0.229$ ($\pm 0.002$)$x$ and $R^2=0.9840$ (organic); V: $y=0.064$ ($\pm 0.001$)$x$ and $R^2=0.9917$(aqueous) versus $y=0.063$ ($\pm 0.001$)$x$ $R^2=0.9962$ (organic). In these equations, $y$ refers to the integrated absorbance and $x$ to the analyte mass. Based on these results the use of aqueous calibration solutions in further studies was justified.

### 3.4. Analytical figures of merit

The limits of detection (LOD) under optimized conditions were 10, 200 and 800 pg for Cu, Fe and V, respectively, calculated according to the IUPAC definition (LOD=3 s/m, where m is the slope of the respective calibration curve and s the standard deviation of ten blank replicates). Since there is no sample blank in the present case, the calibration curve blanks were taken for the calculation. The characteristic masses were 6, 19 and 72 pg for Cu, Fe and V, respectively. It worth mentioning that for Fe and V the instrumental settings were not those of maximum sensitivity but those that permitted the samples to fall within the linear range of the calibration curves. Linearity up to at least 1.5 ng Cu, 15 ng Fe and 60 ng V were observed. The typical sample masses used were 0.10 to 3.00 mg for Cu and Fe and 0.10 to 1.50 mg for V, defining linear ranges varying from 0.003 to 15 µg $g^{-1}$ for Cu, 0.07 to 150 µg $g^{-1}$ for Fe and 0.53 to 600 µg $g^{-1}$ for V. The total determination cycle lasted 4 min, equivalent to a sample throughput of 7 $h^{-1}$ for duplicate determinations.

### 3.5. Accuracy

Certified reference materials (fuel oil NIST 1634c, oil NIST 1085a) and crude oil reference materials (ASTM CO 0403, 0311 and 0504) were used to investigate the accuracy of the method. Moreover, the proposed procedure was compared with independent methods [10,22] in the analysis of real samples. The results are shown in Table 5. No statistically significant difference (ANOVA) was observed between the certified values and the results obtained by the proposed procedure in the analysis of the reference materials, and also between the results obtained in the analysis of the petroleum samples using the proposed and comparative procedures.

## 4. Conclusion

The direct determination of Cu, Fe and V in petroleum samples by ET AAS using a solid sampling accessory, proved to be possible. A Pd+Triton X-100 solution dispensed over the sample was necessary as a modifier, and calibration with aqueous solutions was feasible for all studied elements Although small sample masses were used, good repeatability was observed showing that sufficient sample homogeneity was obtained after just a manual shaking. Weighing petroleum samples at the mg range needed no more skill than weighing the 1 g masses necessary for the alternative procedures. The proposed ET AAS procedure required no sample pre-treatment, avoiding even dilution, and consequently the use organic solvents that are harmful to the human health and environment. The proposed method has the potential to be extended to the determination of other metal traces in petroleum samples, making use of the full detection capability of ET AAS.

## Acknowledgement

The authors thank the Brazilian National Research Council (CNPq) for financial support and Petrobras for kindly giving the petroleum samples.

## References

[1] R.H. Fish, J.J. Komlenic, Molecular characterization and profile identifications of vanadyl compounds in heavy crude petroleums ly liquid chromatography/graphite furnace atomic absorption spectrometry, Anal. Chem. 56 (1984) 510–517.

[2] R.H. Fish, J.J. Komlenic, B.K. Wines, Characterization and comparison of vanadyl and nickel compounds in heavy crude petroleums and asphaltenes by reverse-phase and size-exclusion liquid chromatography/graphite furnace atomic absorption spectrometry, Anal. Chem. 56 (1984) 2452–2460.

[3] N. Márquez, F. Ysambertt, C. De La Cruz, Determination of nickel, vanadium, and sulfur in crudes and heavy crude fractions by inductively coupled argon plasma/atomic emission spectrometry and flame atomic absorption spectrometry, Anal. Chim. Acta 395 (1999) 343–349.

[4] J.G. Reynolds, Ni in Petroleum Refining, Pet. Sci. Technol. 19 (2001) 979–1007.

[5] K.H. Altgelt, M.M. Boduszynski, Composition and Analysis of Heavy Petroleum Fractions, first ed., Marcel Dekker, New York, 1994.

[6] J.L. Fabec, M.L. Ruschak, Determination of nickel, vanadium, and sulfur in crudes and heavy crude fractions by inductively coupled argon plasma/atomic emission spectrometry and flame atomic absorption spectrometry, Anal. Chem. 57 (1985) 1853–1863.

[7] J.G. Speight, Handbook of Petroleum Product Analysis, first ed., Wiley-Interscience, New Jersey, 2002.

[8] M.Y. Khuhawar, S.N. Lanjwani, Simultaneous high performance liquid chromatographic determination of vanadium, nickel, iron and copper in crude petroleum oils using bis(acetylpivalylmethane)ethylenediimine as a complexing reagent, Talanta 43 (1996) 767–770.

[9] C. Duyck, N. Miekeley, C.L. Porto da Silveira, P. Szatmari, Trace element determination in crude oil and its fractions by inductively coupled plasma mass spectrometry using ultrasonic nebulization of toluene solutions, Spectrochim. Acta Part B 57 (2002) 1979–1990.

[10] M.C. González, A.R. Rodriguez, V. González, Determination of vanadium, nickel, iron, copper, and lead in petroleum fractions by atomic absorption spectrophotometry with a graphite furnace, Microchem. J. 35 (1987) 94–106.

[11] M. Bettinelli, P. Tittarelli, Evaluation and validation of instrumental procedures for the determination of nickel and vanadium in fuel oils, J. Anal. At. Spectrom. 9 (1994) 805–812.

[12] G.P. Brandão, R.C. Campos, E.V.R. Castro, H.C. Jesus, Direct determination of nickel in petroleum by solid sampling-graphite furnace atomic absorption spectrometry, Anal. Bioanal. Chem. 386 (2006) 2249–2253.

[13] R.M. Souza, C.L.P. Silveira, R.Q. Aucélio, Evaluation and validation of instrumental procedures for the determination of nickel and vanadium in fuel oils, Anal. Sci. 20 (2004) 351–355.

[14] R.M. Souza, A.L.S. Meliande, C.L.P. Silveira, R.Q. Aucélio, Determination of Mo, Zn, Cd, Ti, Ni, V, Fe, Mn, Cr and Co in crude oil using inductively coupled plasma optical emission spectrometry and sample introduction as detergentless microemulsions, Microchem. J. 82 (2006) 137–141.

[15] C.J. Lord, Determination of trace-metals in crude-oil by inductively coupled plasma mass-spectrometry with microemulsion sample introduction, Anal. Chem. 63 (1991) 1594–1599.

[16] H.M. Al-Swaidan, Simultaneous multielement analysis of Saudi Arabian petroleum by microemulsion inductively coupled plasma mass spectrometry (IC/PMS), Anal. Lett. 27 (1994) 145–152.

[17] H.M. Al-Swaidan, The determination of lead, nickel and vanadium in Saudi Arabian crude oil by sequential injection analysis/inductively-coupled plasma mass spectrometry, Talanta 43 (1996) 1313–1319.

[18] K. Kahen, A. Strubinger, J.R. Chirinos, A. Montaser, Direct injection high efficiency nebulizer-inductively coupled plasma mass spectrometry for analysis of petroleum samples, Spectrochim. Acta Part B 58 (2003) 397–413.

[19] Z. Kowalewska, A. Ruszczynska, E. Bulska, Cu determination in crude oil distillation products by atomic absorption and inductively coupled plasma mass spectrometry after analyte transfer to aqueous solution, Spectrochim. Acta Part B 60 (2005) 351–359.

[20] O. Platteau, M. Carrillo, Determination of metallic elements in crude oil–water emulsions by flame AAS, Fuel 74 (1995) 761–767.

[21] G. Šebor, I. Lang, D. Kolihová, O. Weisser, Effect of the type of organometallic iron and copper compounds on the determination of both metals in petroleum samples by Flame Atomic-absorption Spectrometry, Analyst 107 (1982) 1350–1355.

[22] Standard Test Methods for Determination of Nickel, Vanadium, Iron, and Sodium in Crude Oils and Residual Fuels by Flame Atomic Absorption Spectrometry (Method 5863-B), ASTM International, reapproved 2005.

[23] N.N. Meeravali, S.J. Kumar, The utility of a W–Ir permanent chemical modifier for the determination of Ni and V in emulsified fuel oils and naphtha by transverse heated electrothermal atomic absorption spectrometer, J. Anal. At. Spectrom. 16 (2001) 527–532.

[24] I.C.F. Damin, M.G.R. Vale, M.M. Silva, B. Welz, F.G. Lepri, W.N.L. Santos, S.L.C. Ferreira, Palladium as chemical modifier for the stabilization of volatile nickel and vanadium compounds in crude oil using graphite furnace atomic absorption spectrometry, J. Anal. At. Spectrom. 20 (2005) 1332–1336.

[25] J.B. Stigter, H.P.M. de Haan, R. Guicherit, C.P.A. Dekkers, M.L. Daane, Determination of cadmium, zinc, copper, chromium and arsenic in crude oil cargoes, Environm. Pollut. 107 (2000) 451–464.

[26] Y. Nakamoto, T. Ishimaru, N. Endo, K. Matsusaki, Determination of vanadium in heavy oils by atomic absorption spectrometry using a graphite furnace coated with tungsten, Anal. Sci. 20 (2004) 739–741.

[27] F.G. Lepri, B. Welz, D.L.G. Borges, A.F. Silva, M.G.R. Vale, U. Heitmann, Speciation analysis of volatile and non-volatile vanadium compounds in Brazilian crude oils using high-resolution continuum source graphite furnace atomic absorption spectrometry, Anal. Chim. Acta 558 (2006) 195–200.

[28] S.N. Lanjwani, K.P. Mahar, A.H. Channer, Simultaneous determination of cobalt, copper, iron and vanadium in crude petroleum oils by HPLC, Chromatography 43 (1996) 431–432.

[29] H. Kubo, R. Bernthal, Energy dispersive x-ray fluorescence spectrometric determination of trace elements in oil samples, Anal. Chem. 50 (1978) 899–903.

[30] I. Lang, G.S. Šebor, V. Sychra, D. Kolihová, O. Weisser, Determination of metals in petroleum samples by atomic–absorption spectrometry.2. determination of nickel, Anal. Chim. Acta 84 (1976) 299–305.

[31] G. Šebor, I. Lang, D. Kolihova, O. Weisser, Effect of the type of organometallic iron and copper-compounds on the determination of both metals in petroleum samples by flame atomic-absorption spectroscopy, Analyst 107 (1982) 1350–1355.

[32] J.L. Hammond, Y.I. Lee, C.O. Noble, J.B. Beck, C.E. Proffitt, J. Sneddon, Determination of cadmium, lead, and nickel by simultaneous multielement flame atomic absorption spectrometry in burned and unburned Venezuelan crude oil, Talanta 47 (1998) 261–266.

[33] M.G.R. Vale, I.C.F. Damin, A. Klassen, M.M. Silva, B. Welz, A.F. Silva, F.G. Lepri, D.L.G. Borges, U. Heitmann, Method development for the determination of nickel in petroleum using line-source and high-resolution continuum-source graphite furnace atomic absorption spectrometry, Microchem. J. 77 (2004) 131–140.

[34] M.M. Reyes, R.C. Campos, Determination of copper and nickel in vegetable oils by direct sampling graphite furnace atomic absorption spectrometry, Talanta 70 (2006) 929–932.

[35] P. Grinberg, R.C. Campos, Iridium as permanent modifier in the determination of lead in whole blood and urine by electrothermal atomic absorption spectrometry, Spectrochim. Acta Part B 56 (2001) 1831–1843.

[36] M.T.C. de Loos-Vollebregt, L. de Galan, Zeeman atomic absorption spectrometry, Prog. Anal. At. Spectrosc. 8 (1985) 1985.

[37] H. Gleisner, K. Eichardt, B. Welz, Optimization of analytical performance of a graphite furnace atomic absorption spectrometer with Zeeman-effect

background correction using variable magnetic field strength, Spectrochim. Acta B 58 (2003) 1663–1678.

[38] W.N.L. dos Santos, F. de S. Dias, M.S. Fernandes, M.V. Rebouças, M.G.R. Vale, B. Welz, S.L.C. Ferreira, Application of multivariate technique in method development for the direct determination of copper in petroleum condensate using graphite furnace atomic absorption spectrometry, J. Anal. At. Spectrom. 20 (2005) 127–129.

[39] G.E.P. Box, W.G. Hunter, J.S. Hunter, in: B.B. Neto, I.S. Scarminio, R.E. Bruns (Eds.), Statistics for Experimenters an Introduction to Design, Data Analysis and Model Building, second ed., UNICAMP, S. Paulo, 1996.

ELSEVIER

Spectrochimica Acta Part B 62 (2007) 939–951

SPECTROCHIMICA
ACTA
PART B

www.elsevier.com/locate/sab

Viewpoint

# The determination of trace elements in crude oil and its heavy fractions by atomic spectrometry ☆

Christiane Duyck, Norbert Miekeley, Carmem L. Porto da Silveira, Ricardo Q. Aucélio, Reinaldo C. Campos *, Patrícia Grinberg, Geisamanda P. Brandão

*Departamento de Química da Pontifícia Universidade Católica do Rio de Janeiro, Rua Marquês de São Vicente 225, 22451-900 Rio de Janeiro, Brazil*

Received 5 February 2007; accepted 25 April 2007
Available online 3 May 2007

## Abstract

A literature review on the determination of trace elements in crude oil and heavy molecular mass fractions (saturates, aromatics, resins and asphaltenes) by ICP-MS, ICP OES and AAS is presented. Metal occurrences, forms and distributions are examined as well as their implications in terms of reservoir geochemistry, oil refining and environment. The particular analytical challenges for the determination of metals in these complex matrices by spectrochemical techniques are discussed. Sample preparation based on ashing, microwave-assisted digestion and combustion decomposition procedures is noted as robust and long used. However, the introduction of non-aqueous solvents and micro-emulsions into inductively coupled plasmas is cited as a new trend for achieving rapid and accurate analysis. Separation procedures for operationally defined fractions in crude oil are more systematically applied for the observation of metal distributions and their implications. Chemical speciation is of growing interest, achieved by the coupling of high efficiency separation techniques (e.g., HPLC and GC) to ICP-MS instrumentation, which allows the simultaneous determination of multiple organometallic species of geochemical and environmental importance.

*Keywords:* Trace elements in crude oil; ICP-MS; ICP OES; AAS; Fractionation; Speciation

## Contents

## 1. Occurrences and importance of metals in crude oil and fractions

Crude oil is a complex matrix composed predominantly of saturated and aromatic hydrocarbons, but also containing

---

☆ This paper was presented at the 9th Rio Symposium on Atomic Spectrometry, held in Barquisimeto, Venezuela, 5–10 November 2006, and is published in the special issue of Spectrochimica Acta Part B, dedicated to that conference.

* Corresponding author.
*E-mail address:* rccampos@rdc.puc-rio.br (R.C. Campos).

0584-8547/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.sab.2007.04.013

heteronuclear compounds, emulsified water and minerals [1]. Consequently, metals occur in different organic and inorganic forms. The first organic forms identified, the porphyrins, were described in the beginning of the 20th century as tetrapyrrolic complexes of vanadyl, iron (II) [2] and nickel(II) [3] with structures similar to chlorophyll and heme. These compounds were easily identified by simple spectrographic methods because of their relatively high concentration, specifically in heavy crude oils (e.g., Venezuela Boscan oil) [4]. It was soon observed that the V/Ni ratio was constant in crude oils of common source rocks and dependent on the geological age of the rocks (oils from Triassic or older age showing a value higher than unity) [5], and this ratio was used for tracing source effects [6,7]. Presumably, the metalloporphyrins were derived from chlorophyll-*a*, after the loss of $Mg^{2+}$ at the sediment-water interface and the uptake of $Ni^{2+}$ and $VO^{2+}$ under the prevailing Eh and pH conditions [8]. The high chelating constant resulted in high stability of these compounds, distributed between kerogen and bitumen during oil formation [9]. Studies on the thermal evolution of the major vanadyl complex of deoxophylloerythroetioporphyrin (DPEP) to etioporphyrin indicated a maturity dependence [10,11], thus suggesting the use of these compounds as biomarkers [12]. In contrast to V and Ni, the identification of organic forms of other metals in crude oils was achieved only later, with the advent of hyphenated techniques, e.g., HPLC or GC coupled to AAS or ICP-MS for elemental detection. Porphyrins of Co, Cr, Ti and Zn were identified in oil shales [13] by HPLC–ICP-MS and volatile compounds of alkyl and dialkylmercury were identified by GC–CV–AAS [14] and GC–ICP-MS [15].

Total metal content in crude oils has an extended concentration range, and statistical analysis was the first tool applied to investigate general elemental distribution patterns [16–19].

The analysis of oils worldwide having different viscosities and asphaltene concentrations showed that the more residual the oil, the higher the metal content, being those metal species possibly clustered by heavy molecular mass compounds [18,19]. Alkaline and alkaline earth elements are predominantly associated as carbonates and halides with the emulsified water incorporated into the oil during migration and accumulation in the reservoir [20,21], but their presence can also be the result of contamination from injected water during secondary oil recovery [22]. In sulfate-rich waters, metals are associated with $H_2S$ production through bacterial and thermal reduction of sulfates, which can alter their distributions in crude oils [23].

Crude oil complexity is simplified by separation steps into operationally defined solubility-class fractions. The IP 143 method for asphaltene separation [24] and also a modified ASTM D 2007 method [25] (originally intended for heavy oils above 260 °C) for maltene fractionation into saturates, aromatics and resin (SARA), were applied for the detection of metal partitioning and its implications in crude oil refining and petroleum geochemistry [26–31]. Metals and organometallic compounds distribute roughly in accordance to their volatility. The more volatile species ($Hg^0$, MeHg, DMeHg) are found in the more volatile saturated fraction [32] and vanadyl and nickel porphyrins are observed in intermediate polarity molecular mass fractions of aromatic and N, S, O compounds [4,26]. Most of the non-volatile elements and low volatility species are found in the resin and asphaltene fractions, but mostly in the asphaltenes [31,33,34]. Molecular mass distribution studies using gel permeation chromatography revealed that metals concentrate predominantly in the asphaltene fraction of highest molecular mass and play a major role in asphaltene polarity [35]. The number of trace elements recognized in the asphaltene fraction could be greatly expanded using ICP-MS detection and improved sample introduction methods. It could be shown that this fraction concentrates trace elements up to ten-fold higher than the corresponding crude oil, but still preserving its original elemental fingerprint, allowing new applications in petroleum geochemistry and in environmental studies [18,30].

While advances in refinery processes enable the treatment of high sulfur crude oils, the increasing need for ultra-low sulfur fuels requires the use of low sulfur crudes to reduce the costs of desulfurisation [36]. Metal accumulation in the heaviest polar fractions of crude oils plays a significant role in establishing the refining procedure, since V, Fe, Ni and Mo have both negative and positive effects on product recoveries [37]. High metal content has a general negative effect due to catalyst deactivation by pore clogging, metal deposition, deformation and fissuration of reactors [38]. However, Ni, Co and Mo have a catalytic effect on hydroprocesses and a careful adjustment of the demetallization bed should be made [27]. Most of the metals are separated during deasphaltenation when processes include carbon removal. When hydrotreatment is used, the hydrodemetallization bed and catalyst pore diameter are optimized for a higher recovery and reactor lifetime [39]. Crude oils with high metalloporphyrin content (e.g., Venezuela Boscan oil type) [4,26] are more complicated to treat, since part of it is associated with fractions of intermediate polarity. The process involves hydrogenation prior to demetallization [40], which raises the overall refining costs. Metals and organometallic species are also incorporated during petroleum refining. Nickel, Co, Mo and Ti are constituents of catalysts [41,42]; vanadate and other metal oxides are used during fluid catalytic cracking and $SO_2$ oxidation/removal [43].

Contamination of soils, water and sediments by crude oil and its derivatives is conventionally evaluated by quantification of toxic hydrocarbons (BTX, poliaromatics). More recently, Ni, V and other metals (Cd, Cu, Pb and others) have been included in the analysis of contaminated soils and organisms by crude oil exudates and results show that they can be an important source of contamination for these elements [44,45]. The final refinery products seem to show a higher toxicity compared to crude oil, since metal speciation is altered and new metals are added to the matrix. Experimental studies on enriched fuel combustion show that Se and Hg tend to form volatile species, whereas other elements are associated with the particulate matter (e.g., V, Ni, Co, Zn, Cd, Pb) [46].

Effects on human health are of growing concern [47]. Tetraethyl lead, which was used as an automotive gasoline additive, is a highly toxic compound now forbidden by legislation [48,49]. Additionally, potentially toxic species like selenocyanate (SeCN) are present in wastewater from oil plants, requiring monitoring and water treatment to prevent pollution [50,51].

## 2. Elemental determinations by atomic spectrometry

### 2.1. General aspects

As has been mentioned, crude oil is a complex matrix of varying viscosity and mixed phases (organic, water and particulate matter) and therefore not an ideal matrix for analysis. Determination of metals in crude oils by atomic spectrometric methods requires careful adjustment of experimental parameters [52] as well as sample manipulation before sample presentation to the instrument. Decomposition methodologies can suffer from losses or contamination during sample solubilization procedures [18,53,54], and if aerosol generation is needed, it may be affected by high amounts of salt that cause erosion of the nebulizer orifice and of the sampler and skimmer cones, in the case of ICP-MS. Incomplete desolvation and high concentration of acids result in low mass transport rates of the analyte(s) to the plasma and reduced ion production [55]. Crude oil viscosity and heavy molecular mass fractions are critical in sample introduction methodologies by solubilization in solvents [31] or by micro-emulsions [56], causing nebulizer clogging during aerosol formation and differences in transport efficiencies between standards and samples. Degradation of the torch (ICP OES and ICP-MS) and the sampler and skimmer cones (ICP-MS) is also observed when argon–oxygen plasmas are used to minimize carbon build-up [57–59]. These problems are avoided or minimized in certain direct sample introduction methods, such as ETV–ICP-MS [60].

Together with a proper sample introduction technique, multiple calibration curves are often employed in multielemental techniques (ICP OES and ICP-MS) to cover the wide range of metal concentrations in crude oils, from below ng g$^{-1}$ to hundreds of µg g$^{-1}$ [4,18,30]. Internal standardization is not only used for instrumental drift correction, but also to account for differences between blanks, calibration standards, and samples. For the most complex matrices, the analyte addition calibration is the only method that will yield reliable results [31].

Spectral interferences inherent to the analysis of highly organic loaded samples by ICP techniques may occur, requiring the use of alternative wavelengths or isotopes of lower abundance [57,61,62], e.g. $^{26}$Mg (11.01%) instead of $^{24}$Mg (78.99%), the latter interfered by $^{12}C_2^+$ (see further below). Spectral interferences of argon and carbon species are less critical in ICP OES since they can be minimized or avoided by proper line selection and/or observation height [61]. Nonetheless, they contribute to the overall background elevation. ICP OES is, however, limited by its reduced detection power (µg g$^{-1}$ range) for most elements, which restricts its applications in geochemical and environmental studies [28,63].

Due to its nature, good selectivity is associated with AAS methods. Flame AAS (FAAS) is a well established and accessible technique, less prone to spectral interferences in comparison to other spectrometric techniques. However, AAS essentially remains a monoelemental method, although the recent appearance of a continuum source FAAS instrument [64] makes sequential analysis possible, similar to those performed with sequential ICP OES instrumentation. Nevertheless, detection limits for a series of elements is still poor for many applications in crude oil analysis. In addition, although the great thermal capacity of the flames used in FAAS with high enough temperatures for the complete atomization of many elements, different responses for different species for the same element may be observed in the analysis of samples such as oil dissolved in organic solvents. Thus, a careful control of the atomization (flame) conditions and of sample introduction parameters must be performed if oil dilution in organic solvents is the sample pre-treatment of choice. Electrothermal atomization in a graphite furnace (ET AAS) and chemical vapor generation (CVG) techniques overcomes the sensitivity limitations of FAAS. Nevertheless, while for CVG techniques samples must be reduced in aqueous medium after mineralization or extraction (with few exceptions) [65,66] ET AAS techniques have the potential to accept samples as they are, minimizing or even dispensing with sample pre-treatment. However, carefully optimized furnace operation conditions must be used for either atomization from platforms or directly from tube wall. The use of improved atomizers, such as the transversally heated graphite atomizer (THGA), is recommended in order to improve pyrolysis and atomization efficiency, minimizing build-up of sample residues in the atomizer.

All of these facts make the analysis of crude oil and fractions by AAS and ICP techniques a challenge. In the following sections, different approaches to overcome these difficulties will be reviewed and critically discussed.

### 2.2. Analysis after sample decomposition by ashing

Matrix decomposition results in aqueous solutions that can be, in principle, analyzed by any spectrometric technique. Ashing of the crude oil followed by dissolution of the ash in mineral acids was the first decomposition method used, prior to the determination of metal content by FAAS or ICP OES [19]. About 5 to 10 g of crude oil is usually placed in a quartz beaker or a platinum crucible and heated over a Bunsen gas burner to achieve total ashing of the material. Although this procedure is still largely employed in industry, it is time-consuming (about a day-long), and dangerous due to the evolution of toxic vapors and the usually low flash point of petroleum. The simultaneous use of mineral acids (e.g., $H_2SO_4$, $HNO_3$, HCl) may be an advantageous alternative, but the main drawback of this method is the loss of elements by volatilization (Hg, halides of As, Se, V and Pb), the contamination by the larger amount of reagents used and the open environment, and the precipitation of sparely soluble salts during the final dissolution step (e.g., sulfates of Pb, Ba and Sr) [18]. Since acid decomposition of the matrix in open vessels avoids the safety risks characteristic of the dry ashing procedure and allows the simultaneous processing of a high number of samples, it is still largely used [28]. Such a procedure is generally performed with larger volumes of oxidizing acids (e.g., 10 mL of acid per 0.5 g of sample) and the time for complete decomposition is long (up to several days).

Contamination and losses are overcome by the use of acid decomposition in closed vessels, performed in conventional heating systems (such as the Parr reactor [67], or its improved version, the High Pressure Asher [68]) and microwave-assisted heating [69]. All of these procedures provide final light-colored and transparent solutions in contrast to the open vessel procedures, indicating that carbon has been more efficiently removed. Focused microwave-assisted heating decomposition has been developed for on-line decomposition and low contamination of geological samples [70]. This is a promising technique for the decomposition of crude oil, and more specifically its heavy fractions (asphaltenes and resin), permitting automation of the processing; however, matrix effects and spectral interferences due to residual carbon content should be evaluated [71]. Additional oxidative reagents, such as $H_2O_2$ used after acid decomposition, are necessary for better carbon removal [72]. All of these methods have a poorer reproducibility of the results when compared to simple dilution in organic solvents or to micro-emulsion based methods.

Unfortunately, only a very limited number of appropriate certified reference materials (e.g., NIST 1634b and 1634c) are available for the validation of decomposition methods for heavy crude oil and its fractions. A more recently available decomposition system, which uses pressurized quartz vessels, the High Pressure Asher (HPA), considerably reduces the residual carbon content; however, the higher amounts of reagents used (e.g., 10 mL of $HNO_3$) require an additional vaporization step to get rid of excess $HNO_3$, especially when ICP-MS is employed for elemental detection [73].

External calibration procedures in atomic spectrometric techniques for the analysis of crude oil after decomposition are similar to those employed for solutions of varying acidity (1 to 10%): they may use analytical solutions prepared in the same medium as the blank solution (AAS) and/or by the corrections of an internal standard(s). The need for the “analyte addition calibration” depends on several factors, including the carbon content and viscosity of the matrix and, obviously, on the required accuracy and repeatability of the results. For a given ICP instrument, detection limits are generally improved when desolvation devices are used, such as ultrasonic nebulizers and/or membrane separators [74].

In ICP-MS, spectral interferences may occur as crude oil contains a high number of elements in the low concentrations range (ng $g^{-1}$). Doubly charged ions ($Ba^{2+}$ at m/z 69, Ga) are also potential interferents encountered during the analysis of decomposed solutions of high salinity. Polyatomic interferences generally arise from the reaction products of argon with major matrix components (e.g., Na, Ca, Sr) or residual carbon [75]. Ar-species of Na, Cl and Ca interfere respectively at m/z=63 (Cu), m/z=75 (As) and m/z=78, 82 (Se); carbon species ($C_2$, ArC) interfere at m/z=24 (Mg) and m/z=52, 53 (Cr). In oils of high sulfur concentrations, additional interferences from S species may superpose (e.g., $^{32}S^{32}S$ and $^{34}S^{32}S$ species on Zn at m/z 64 and 66). Frequently, polyatomic interferences are minimized or avoided by the choice of alternative isotopes and/or the application of desolvation systems for reducing the solvent load [74]. Advances in ICP-MS instrumentation are likely to provide additional solutions to the problem of polyatomic interferences, with progress in dynamic reaction/collision cell technologies and high resolution spectrometers [76]. In the case of DRC–ICP-MS, the species are destroyed by collision with a reactive gas ($CH_4$, $NH_3$) and improvements on major interferences are achieved at a relatively low-cost [77]. HR-ICP-MS has, however, the advantage of resolving most spectral interferences [55], but instruments seem to be less robust and are more expensive.

Flame, electrothermal furnace as well as chemical vapor generation AAS are well suited for trace-metal determinations in oil after ashing. Indeed, ashing of a sufficiently large sample mass may compensate for the comparatively lower FAAS sensitivity, although a longer analysis time is needed. However, losses of Ni and V, present as volatile compounds (metalloporphyrins), may occur if adequate care is not taken. For instance, Udoh et al. [78] and Platteau and Carrillo [79] suggest the use of linear alkylbenzene sulfonic acids for stabilizing these compounds. The former authors remember that the addition of sulfur containing compounds has long been the strategy of choice for avoiding losses of Ni and V by volatilization during ashing. According to Platteau and Carrillo [79], the simultaneous ignition of the oil–acid mixture, while it is still boiling, prevents volatilization losses for Fe, Na and Ni, eliminates the coke residue and reduces the ashing time, thus allowing the achievement of results similar to those obtained by standard methods for the same samples. Ashing procedures based on the use of sulfuric acid for the trace-metal determination in oil are also suggested in the literature and they were recently re-approved as standard methods for the determination of Ni, V, and Fe in crude oils and residual fuels [80]. Infrared heating using a “mini-ash” device is also proposed [81]. An overview of ashing procedures using sulfur compounds can be found in Sychra et al. [82]. Ashing followed by fusion, and post-determination by ICP OES and AAS is also proposed as standard methodology for the determination of silicon and aluminum in fuel oils [83]. In general, hydrochloric acid is the acid of choice for the final dissolution of the mineral residue.

In the case of mineral acid decomposition, the acid, salt and carbon content of the final solution to be presented to the instrument is not as critical in AAS techniques as for ICP-MS. This may lead to simpler sample dissolution procedures and lower dilution factors. EPA method 3031 [84] proposes the use of an initial oxidization with an excess of $KMnO_4$ in the presence of sulfuric acid, followed by heating and further mineralization with $HNO_3$ and an excess of $HClO_4$. FAAS, ET AAS and ICP OES are indicated for the instrumental determination of a number of trace elements. If ET AAS is the technique of choice, the elimination of the excess $HClO_4$ is recommended. In the case of As, the crude oil samples were digested with sulfuric acid and $H_2O_2$ under reflux, followed by measurement of As in the diluted digest by hydride generation AAS [85]. An acid digestion procedure with a $HNO_3$–$H_2SO_4$ mixture under reflux is proposed by Turunen et al. [86]. The whole procedure takes 2–3 h and special care must be taken in the first digestion steps, due to risk of explosion. The determination of As, Cd, Cr, Cu, Mn, Ni, Pb and V was performed by ET AAS, a technique that can deal well with residual carbon if STPF conditions are followed, with the special attention to the background correction system. Acid digestion efficiency may be enhanced by microwave heating. In this way, EPA method 3051 [87] uses the digestion of oils and other samples with 10 mL of nitric acid; for 0.5 g-samples, only 10 min of heating is, in principle, necessary. FAAS, ET AAS, ICP OES and ICP-MS are indicated for the instrumental measurements. Alvarado et al. [88] optimized a method for the microwave digestion of various crude oil samples, investigating various proportions of nitric and sulfuric acids. The solutions obtained were analyzed by ET AAS for Cr, Cu, Fe, Mn, Ni and V and for Na and Zn using FAAS. Analyte addition had to be used for accurate results. As pointed out by Bettinelli et al. [89] and Krachler et al. [90], the use of microwave digestion in a high-pressure closed vessel reduces sample decomposition time because higher temperatures can be achieved, leading to faster reaction times and the decomposition of difficult samples, besides other advantages already pointed out in this review. In an attempt to determine As, Sb and Se in oily wastes by hydride generation AAS, Campbell and Kamet [91] stated that any residual organic matter may cause difficulties, especially if the analytes are present as organometallic species. They overcame these difficulties by complete oxidation of the organic matrix after solvent extraction using microwave-assisted digestion in a closed system. The use of focused microwave-assisted heating for oil digestion was critically investigated by Costa et al. [71]. The authors conclude that a focused-microwave oven designed with one magnetron and six reaction flasks led to different degrees of decomposition, depending on operating conditions, such as sample cavity position and applied power. The consequent variation in the residual carbon content could affect the quantification of elements susceptible to carbon argide isobaric interferences when using ICP-MS.

Extraction appears to be an alternative to mineralization for the determination of As in crude oil [92]. Extraction was performed with boiling water or boiling aqueous nitric acid (concentration 0.25 to 2.5 M), followed by the mineralization of the extracts with concentrated nitric/sulfuric acid, and reduction of the arsenate to arsine in a hydride generator. Viscous hydrocarbons, such as fuel oil, must be dissolved in xylene for the extraction to be successful. In the case of ICP-MS detection, the direct determination of As in 1–10% $HNO_3$ matrices was possible using 4% (v/v) ethanol to reduce the ArCl interference [93]. In hydride generation techniques, the separation of the analyte from the matrix and its interference-free measurement is intrinsically associated with the method. However, attention must be paid to some potential interfering species, such as $Ni^{2+}$, in order to avoid their interference in the hydride generation process in the liquid phase [94]. An extraction method is also proposed for the determination of V in petroleum crudes, based on the synergistic extraction of the V(V)-5,′-methylenedisalicylohydroxamic acid (MEDSHA) complex with a 0.5 M tributyl phosphate (TBP) solution in isobutyl methyl ketone (IBMK), followed by FAAS [95]. Table 1 summarizes matrices

Table 1
Elemental determination in crude oil and heavy fractions by ICP-MS and ICP OES

| Matrix | Element(s) determined | Solubilization procedure | Technique | Reference |
|---|---|---|---|---|
| Crude oil | V, Ni, Co, Cu, Mo, Fe, Mn, Zn, Ti | Ashing decomposition | ICP OES | [19] |
| Crude oil | S, Al, V, Ni, Co, Fe, Cu, Zn, Ba, Mo | Micro-emulsion | ICP OES | [17] |
| Crude oil, saturates, aromatics, resin, asphaltenes | V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Ga | No | ETV–ICP-MS | [113] |
| SRM residual fuel oil 1634c, crude oil, saturates, aromatics, resin, asphaltenes | Ag, Al, Ba, Cd, Co, Cu, Fe, La, Mg, Mo, Mn, Na, Ni, Pb, Sn, Sr, Ti, Pb, U, V, Zn, Y, La–Lu, Au, Pd, Pt, U, Th | Microwave acid decomposition in closed vessels | ICP-MS | [18,30] |
| Saturates, aromatics, resin, asphaltenes | Co, Cr, Cu, Fe, Mo, Mn, Ni, Sr, V, Zn | Acid decomposition in open vessels | ICP OES | [28] |
| Crude oil | Hg | Combustion in Carius tubes | ICP-MS | [53] |
| SRM residual fuel oil 1634b | Ag, Al, As, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mo, Na, Ni, Pb, Sb, Sn, Sr, Ti, Tl, U, V, Zn | Microwave acid decomposition in closed vessels | ICP-MS | [72] |
| SRM residual fuel oil 1634b | Na, Mg, Al, Ti, Cr, Fe, Ni, Co, Cu, Ag, Pb | No | LA–ICP-TOF-MS | [114] |
| Crude oil | Li, Al, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Sr, Mo, Ag, Cd, Sn, Sb, Ba, Pb | Micro-emulsion | ICP-MS | [56] |
| Crude oil | Mo, Zn, Cd, Ti, Ni, V, Fe, Mn, Cr, Co | Micro-emulsion | ICP OES | [112] |
| Crude oil cut (naphta) | Na, P, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, As, Y, Mo, Cd, Sn, Sb, Hg, Pb, Bi | Dilution in xylene | ICP-MS | [98] |
| Synthetic crude oil | As, Cd, Hg, Ni, Pb, V | Dilution in xylene | DIHEN–ICP-MS | [105] |
| SRM residual fuel oil 1634c, crude oil, saturates, aromatics, resin, asphaltenes | Ag, Al, Ba, Cd, Co, Cu, Fe, La, Mg, Mo, Mn, Na, Ni, Pb, Sn, Sr, Ti, Pb, U, V, Zn, Y | Solubilization in toluene and ultrasonic nebulization | ICP-MS | [31] |
| Crude oil, gasoline, distillation cuts and residue | Cu | Ashing, microwave-assisted and combustion decompositions | ICP-MS | [54] |
| Crude oil (oil spill) | Cd, Cr, Cu, Pb, Mn, Ni, V, Zn | Microwave-assisted acid decomposition | ICP OES | [63] |

analyzed by ICP OES and ICP-MS using different sample preparation procedures.

### 2.3. Direct sample introduction strategies

Direct introduction of crude oil and derivatives into ICP instruments has been performed by two techniques. The first uses sample solubilization in an organic solvent (e.g., toluene, xylene, kerosene) and the second is an emulsification procedure in aqueous solutions in the presence of emulsifiers.

Solubilization of crude oil and derivatives in solvents is by far the most studied and used direct introduction technique for ICP instruments and is widespread in the industry [58,96–98], essentially, because it is a fast and accurate technique. Its advances follow closely the improvements in sample introduction systems and ICP instrumentation. Crude oil and derivatives dissolve in solvents like toluene, xylene chloroform and kerosene. In early studies, the Meinhard nebulizer was used in combination with a Scott spray chamber to introduce these solvents into ICP OES instruments. The solvent plasma load (SPL) was identified as a critical problem, which causes instability and sometimes extinction of the plasma and raises the background level due to the strong $C_2$ green and other emissions (e.g., CN, OH) [57,61]. Desolvation of the aerosol was achieved through a −10 °C refrigerated chamber, which was the temperature calculated for a minimum SPL for low vapor pressure solvents like chloroform, and background level was reduced by use of higher observation heights (15 mm) and higher plasma temperatures (1.5–2 kW of forward power) [57]. When the technique is applied to ICP-MS, another critical effect observed is the deposition of carbon on the sampler and skimmer cones, and a higher level of carbon interferences [99]. The problem was overcome by $O_2$ addition to the argon [100] but new interferences appeared due to the presence of oxygen: e.g., ArO at m/z 56 (Fe), $CO_2$ at m/z 48 (Ti). Chloroform could not be used due to Cl interferences (ClO and ArCl) at m/z 51 (V) and 75 (As), respectively. Determination of several elements in SRM NIST 1634b was performed with acceptable accuracy [62]. The use of a heated tube instead of refrigeration for aerosol desolvation was more efficient in reducing the SPL and pointed to the limitation of the Meinhard/Scott refrigerated system [101].

The advent of ultrasonic nebulization devices, which combined temperature and refrigeration along with a membrane desolvator, finally retired the Meinhard nebulizer for this purpose [58,96]. A universal calibration for solvents was proposed based on *n*-hexane with good recoveries [97]. Calibration was achieved using organometallic standards in oil (Conostan, Conoco, USA). However, memory effects and higher dispersion of the droplet diameter were observed [102,103], as well as the loss of volatile species of Pb and Hg during analysis of condensates and naphta [104]. For the analysis of crude oil and fractions, the USN device was used without heating, and good accuracy was obtained for determination of metals in fuel SRM by ICP-MS [31]. Direct injection nebulizers (DIN) and micronebulizers appear as the next path for multielemental analysis of crude oil and derivatives diluted in solvents. The analysis of naphta was successfully achieved with a DIN [98] and a high efficiency DIN (DIHEN) [105] using oxygen in the nebulizer gas flow, with solution uptake rates as low as 60 and 10 μL $min^{-1}$, which reduced considerably the carbon and oxygen levels in the plasma. The DIN methodology [98] allowed the determination of volatile elements like As with limits of detection lower than 0.1 ng $g^{-1}$. The solutions were weekly stable for As. The DIHEN was used for the determination of Hg and its organic species in hexane, with similar detection limits and without significant memory effects [106]. SPL can also be lowered using micronebulizers from which the new Teflon ones showed improvements for the liquid/gas interaction and are promising tools for solvent introduction [107,108].

The availability of DRC- and CC–ICP-MS instruments and the proper choice of reactive gases are also promising means for the removal of major spectral interferences caused by solvent introduction into the plasma in the case of quadrupole mass spectrometers [77,108].

Solubilization of crude oil by water-in-oil (w/o) or inverse (o/w) emulsion formation has gained interest because it allows the determination of elements in the organic phase using inorganic aqueous standards. The first study of o/w micro-emulsion used a non-ionic surfactant to assist dispersion of oil as organic micelles in water. Sample introduction into ICP-MS was performed with a Meinhard nebulizer/Scott spray chamber system refrigerated at 8 °C [56]. The solutions were monthly stable, and carbon interferences on m/z 24 (Mg) and 56 (Fe) were considerably reduced, allowing the determination of these elements even in the presence of the organic phase (1,2,3,4-tretrahydronaphtalene: Triton X-100). Good results were obtained for SRM NIST 1634c; however, limitations were observed with heavy crude oil emulsions, which showed a signal drop of the internal standard of up to 50% [56]. Triton X-100 emulsions were also successfully applied to the determination of V, Co, Ni, As, Hg and Pb in naphta [109]. Another non-ionic emulsifier, polyoxyethylene nonylphenyl ether (Igepal), was preferred for heavy crude oils because of his slightly higher hydrophile–lipophile balance number (Igepal CO-720 = 14.2, instead of 13.5 for the Triton X-100), which enabled higher solubility in water through hydrogen bonding [110]. In order to reduce solution viscosity, the same authors added xylene, without using a refrigerated spray chamber during sample introduction, which compromised the limits of detection because of incomplete combustion of the organic matter [111]. Detergentless emulsions were reported for the determination of elements in crude oils by ICP OES using acidified water for element stabilization and propan-1-ol as a co-solvent, with addition of oxygen to the nebulizer gas flow [112].

Direct introduction of crude oil and fractions in ICP-MS has also been investigated using special introduction devices, such as electrothermal vaporization (ETV) and laser ablation (LA). Ten elements in crude oils and fractions were determined by ETV–ICP-MS for the study of oil migration [113], using 10–15 μL of sample and a vaporization temperature of 2550 °C. Recovery values for the crude oil fractions were not satisfactory for six elements, which raise serious doubts about the overall methodology. However, ETV–ICP-MS is an interesting technique for heavy crude oils and fractions like resin and asphaltenes, because of the total removal of the matrix, but possible interferences from the volatilized carbon of the furnace should be further investigated.

Laser ablation was also investigated for the direct introduction of SRM NIST 1634b into ICP-TOF-MS [114]. The laser was a nanosecond Nd-YAG working at 266 nm wavelength. The ablation cell was modified for higher efficiency of analyte transport to the plasma and narrower transient signal profile. Calibration was achieved in wet plasma conditions introducing simultaneously the aqueous calibration solutions through a Meinhard nebulizer/Wu–Hieftje vertical-rotary spray chamber system, or in dry plasma conditions using organometallic standards. The technique showed high sensitivity for multielement determination and good accuracy, however, chemical fractionation was not investigated.

Oil dilution in an appropriate solvent followed by direct analysis by FAAS appears as a natural and simpler alternative to sample mineralization and has been long applied. The solvent must offer a stable and non-luminous flame, low toxicity and, of course, be able to completely dissolve the sample. The final solution must be homogeneous and stable in time. For instance, use of FAAS after dilution of the oil with an organic solvent is proposed in an ASTM standard test method for the determination of Ni, V, Fe, and Na in crude oils and residual fuels [80]. Dilution in xylene was used in the comparative determination of Ni and V in crudes and heavy crude fractions by ICP OES and FAAS [115]. Solubilization with MIBK was used in the analysis of crudes and its burning residues for the determination of V [116] as well as Cd, Pb and Ni [117], also by FAAS. The authors note, however, that analyte addition calibration with organometallic standards is necessary for accurate results. A toluene–acetic acid mixture was used as solvent for the dilution of petroleum crudes and further determination of Ni, Cu, Zn, Na, Pb, Cd, and Fe by FAAS. Calibration was performed with inorganic salts and by analyte addition. Systematic errors between the proposed procedure and a comparative one consisting of sample dilution in xylene and organometallic calibration ranged from 2 to 25% [118]. As early as 1981, Sychra et al. [82] presented a detailed discussion on the flame analysis of crude oils, heavy petroleum oils and residues using dilution methods. The authors reviewed the application of this procedure up to that date, and pointed out problems that must be addressed: Hardly a single solvent or a solvent mixture is able to completely dissolve all the different kinds of oil samples. Thus, dissolution efficiency varies for each class of oil sample, with highly paraffinic oils presenting the major difficulties. Also, different organic compounds of the same element present different responses in the flame, no matter if an air or a nitrous oxide acetylene flame is used. This leads to calibration difficulties as well as different responses depending on the organometallic composition of the sample [119]. Matching the analytical solutions' and sample's physical properties is also a challenge. In short, the authors state that external calibration should only be used for a rapid and rough estimation of the metal content; analyte addition calibration being more accurate due to the leveling effect of the matrix on some of the physical–chemical properties involved in the atomization process. The authors recommended the accuracy being checked with the dilution method for each set of samples by comparing the results with those achieved using a wet-ashing procedure. Nevertheless, Bettinelli and Tittarelli [120] validated a procedure for the determination of Ni and V in fuel oil based on the 1+9 dilution with xylene and calibration with Conostan organometallic standards, using base oil for matching the viscosity or fuel oil with known metal content. Nickel was determined in air–acetylene flame and a nitrous oxide–acetylene flame was used for V. The procedure was compared with a series of independent methods in the analysis of six samples with different metal contents. Results very close to the consensus values were observed. The authors state that the better repeatability and reproducibility observed in comparison to other similar methods came from the more detailed specification of experimental parameters, such as checking the instrumental performance, alignment of the burner head and radiation beam, and selection of the aspiration rate. A limited aspiration rate of the organic solution ($<2$ml min$^{-1}$) was recommended.

The association of sample dilution with ET AAS would, in principle, overcome problems encountered with determinations by FAAS. Its higher sensitivity would permit the determination of less concentrated elements and the high temperatures during the pyrolysis step would eliminate most of the matrix and bring the analyte to the same chemical form, avoiding differences in sensitivity due to different compounds. Moreover, the larger dilution factor permitted due to the higher sensitivity would reduce the chances of matrix interferences. In this way, Bruhn and Cabalin [121] proposed the determination of Ni in gas oil after dilution with xylene. However, analyte addition had to be used and analyte solutions prepared from different Ni organocompounds led to different sensitivities. The choice of the adequate Ni compound for calibration had to be decided after comparison with the reference wet-ashing results obtained with the FAAS methodology. The author also pointed out problems related to analyte solution stability at the µg L$^{-1}$ range. A discussion on possible losses of volatile Ni species during pyrolysis is also presented, as well as the promising use of chemical modifiers to overcome such losses. Taking all findings into consideration, good concordance between proposed and reference methods was obtained. The problems reported by Bruhn and Cabalin [121] summarize all factors that must be considered in solvent dilution–ET AAS approaches and agree with the critical observations, presented by Sychra et al. [82], on early ET AAS work. Vanadium, Ni, Fe and Pb were determined in crude and fuel oil following dilution with xylene and MIBK [122]. The authors report good agreement with certified values for the analysis of SRMs and analyte addition calibration curves showed the same slope as those obtained with organic analytical solutions. No modifier was used, even for the determination of a volatile element such as Pb. Bermejo-Barrera et al. [123] observed that xylene dissolution and dry calcination were equivalent for the determination of V in petroleum samples by ET AAS. The authors propose that the crude oil must be so strongly diluted that matrix interference is eliminated. The behavior of a series of chemical modifiers for the determination of V in a water and oil matrix was studied by Thomainidis and Piperaki [124]. Since a longitudinally heated furnace was employed, no platform was used, but all other STPF conditions were followed. In the determination of V in a multielement standard diluted with MIBK, Pt as modifier enhanced the pyrolysis temperature from 1000 °C to 1400 °C, with improvements in sensitivity. No difficulties on mixing the aqueous modifier with the organic sample is reported, as well as no application to real samples. The determination of Cd, Cr and Cu in crude oils was also performed by Stigter et al. [85]. Atomization from a platform, Zeeman-effect background correction as well as oxygen ashing during the pyrolysis step was used. For Cd, the authors diluted the samples with carbon tetrachloride. Due to the toxicity of this solvent, xylene was used for the other metals. The authors pointed out the instability of samples and organometallic standards in these media, and finally changed to a 4:1 v/v mixture of toluene and acetic acid as solvent. Cadmium, Cu, and Cr were determined by ET AAS and Zn by FAAS. The authors noted that the analytical solutions (Conostan standards diluted in the solvent mixture) as well as the diluted sample should be freshly prepared, due to potential lack of stability after 48 h. The efficiency of the sample homogeneity procedure was also addressed and relative standard deviations ($n=10$) up to 26% for Cd and 7% for Cr were observed. Validation was performed by comparison with wet-ashing methods, and in contrast to the agreement observed for other elements, significantly lower results for Cd were presented. It is worth noting that no modifier was used. A tungsten-coated graphite furnace was used for the determination of V in heavy fuel oils [125]. Sulfur interference was studied in detail. These studies showed that the solution presented to the instrument should contain less than 1% sulfur. Good concordance between the results obtained from the proposed (sample dilution with tetrahydrofurane + light oil, 1 + 1) and comparative procedures was reported.

The use of emulsions for the dilution of organic liquid samples is an alternative to the dilution with organic solvents, with some potential advantages. In the case of FAAS, less organic solvent is presented to the flame, while for ET AAS the use of modifiers is facilitated and the sample and analytical solutions are more stable at the µg $L^{-1}$ level. Emulsification retains the simplicity of the dilution process and permits the use of inorganic standards for calibration. The determination of Ni in fuel oil by FAAS using 4% v/v oil-in-water emulsion is described [126]. The oil sample is diluted in water in white spirit emulsion. An Ni aqueous working solution dispersed in the same medium is used for calibration. For matching the viscosity between samples and analytical emulsions, water and lubricating oil are respectively added to these dispersions. Comparison of the slopes of analyte addition curves and analytical curves prepared in the same way as the sample confirmed the possibility of external calibration. The comparison with a reference method led to concordant results. Nickel and V were determined in naphtha and fuel oils after emulsion formation by ET AAS using W–Ir as permanent modifier [127]. The oil samples were diluted in toluene, and this solution was emulsified by stirring with 3% Triton X-100 in water. Calibration was performed with organometallic standards prepared in the same way. The emulsions were stable from 20 to 50 min. Different permanent modifiers were studied under STPF conditions. The W–Ir permanent modifier proved its utility for the determination of Ni, while for V the untreated tube appeared to be more suitable. Excellent agreement between found and certified results was observed in the analysis of two SRM. Burguera and co-workers [128] determined Cr in heavy crude oil and in a bitumen-in-water emulsion by ET AAS after sample emulsification. The optimum sample emulsion composition was 7:3 v/v (w/o) + 0.2% w/w of a non-ionic surfactant, which was 1 + 8 diluted with a 0.2% w/w solution of the surfactant. STPF conditions permitted the calibration with aqueous analytical solutions, and good concordance with a comparative procedure was obtained. Emulsification was used in a detailed study on the optimization of the Ni determination in petroleum using both line source and high resolution continuum source ET AAS [129]. After verifying that samples and analytical solutions diluted with xylene and MIBK were not useful due to their poor stability, the authors stabilized samples and analyte solutions as an o/w emulsion consisting of xylene, Triton X-100 and water. An ultrasonic bath was used in the emulsification process and the mixture was further homogenized just before the measurement by manually flushing them with a micropipette. The authors observed that significant Ni losses occur at pyrolysis temperatures as low as 500 °C, most probably due to the presence of volatile Ni species. Thus, good concordance between found and expected results could be achieved only if a pyrolysis temperature of 400 °C was used. The BG-correction ability of the continuum source AAS was able to deal with the high BG values observed with such a low pyrolysis temperature. Similar stabilization difficulties were experienced by Aucélio and co-workers [130] in the determination of V in the asphaltene petroleum fraction. A solution of asphaltene in dichlorethane was obtained as the result of the fractionation procedure, and this solution showed clear loss of V as a function of the sample solution storage time (formation of insoluble V species or/and their adsorption of on the wall of the storage vial) as well as during ET AAS analysis due to the formation of volatile compounds. The solution was stabilized by simply mixing with propan-1-ol and 6 mol $L^{-1}$ $HNO_3$, forming a detergentless micro-emulsion. The micro-emulsion is spontaneously and immediately formed, and its stability was confirmed up to 80 h. Calibration was performed by spiking inorganic V in the same micro-emulsion medium. The analysis of the asphaltenic fraction of a fuel oil SRM showed a coherent result taking into consideration the certified value for V in the whole fuel oil. Damin and co-workers [131] investigated the use of Pd as a chemical modifier for the stabilization of the volatile Ni and V compounds in oil samples, since the BG ability of line source ET AAS was not able to correct the high BG values imposed by the necessary low pyrolysis temperatures if no modifier was used. The oil sample was stabilized as an o/w emulsion, whose composition was optimized by a multivariate method. The use of Pd (20 µg) as chemical modifier permitted pyrolysis temperatures high enough to lead to low BG without any analyte loss. Good agreement was observed between found and expected values, using analytical solutions prepared in the same way as the samples spiked with inorganic standard solution.

Another approach is direct sample introduction for ET AAS, in which the sample is used without any further treatment other than homogenization [132]. This technique can also be used for highly viscous liquids, and has applied to the determination of Ni [133], Ni and V [134] as well as Cu, Fe and V [135] in oil samples. This approach brings the advantage of no chemical sample pre-treatment, eliminating contamination and losses related to this step. The adequate use of modifiers avoids analyte losses during the pyrolysis step. The addition of Triton X-100 to the modifier solution improved its efficiency, probably due to a more effective interaction between the aqueous modifier solution and the oily sample. Calibration curves with aqueous analytical solutions were used, and the results for oil samples and SRM were concordant with those derived from conventional procedures.

### 2.4. Speciation of elements in crude oil and its fractions

The hyphenation of HPLC and GC with elemental detectors, such as ICP-MS, ICP OES, AAS and AFS, permits the determination of elements in their organometallic form. The chromatographic techniques are used to separate and also identify the different forms, while the atomic spectrometric detectors are used for quantification, using adequate standards. In a few early studies [136,137], HPLC was interfaced with ET AAS in order to investigate the presence of different Ni and V compounds in heavy crudes and asphaltenes as a possible *fingerprint* of the oil. However, ET AAS is not well suited as a specific detector in hyphenated techniques, due to its stepwise characteristic. FAAS [138] was used in the comparison of three analytical methods to isolate and characterize V and Ni porphyrins from heavy crude oil. However, the use of FAAS as a detector in hyphenated speciation analysis fails, in general, due to its low sensitivity. Recently, Lepri et al. [139] proposed a speciation (fractionation) analysis between volatile and non-volatile Ni and V compounds in crude oil based on their different characteristics during the ET AAS pyrolysis step. Partial information on the nature of these compounds could be obtained. However, speciation analysis with a much higher level of information can be performed by hyphenating HPLC to an ICP-MS, since it does not require a heated interface and delivers sample in a liquid state at flow rates of around 1 mL $\text{min}^{-1}$, compatible with most nebulizers. The identification and quantification of metalloporphyrins was performed by HPLC–ICP-MS using a reversed phase $C_{18}$ column [13,140]. Introduction of the mobile phase into the ICP does not necessarily need the presence of oxygen in the nebulizer gas, depending on: (i) if an oxygenated solvent like methanol is used, instead of aromatic or chlorinated solvents, and (ii) the percentage of solvent in the mobile phase. Capillary electrophoresis has also been employed for the separation step [141]; however, the technique is limited to ionizable metalloporphyrin (with a COOH function), otherwise the separation does not occur, and also by a loss of sensitivity due to the reduced electroosmotic flow (nL $\text{min}^{-1}$), inherent to this separation technique. If HPLC is the method of choice for high boiling point organometallic compounds, GC is the one for volatile species. Mercury species were successfully determined by GC–CV–AAS [14] and GC–ICP-MS [15] in natural gas condensates and require a cryogenic trap for retention of MeHg and DMeHg prior to GC separation.

## 3. Conclusions

From a general point of view, there is not a unique methodology for determination of elements of interest in crude oil and its derivatives. The choice of the methodology should be based on the matrix, on the element (or series of elements) to be determined, and on the objectives of the analysis. Decomposition methodologies are time-consuming; however, they are generally more robust and accurate than direct sample introduction after sample dilution in organic solvents. This results in more complex matrices. Decomposition by wet-ashing is the most frequently applied technique, even in standard methods. Losses may be avoided by adding a sulfur containing compound, but strict control of the ashing temperature must be observed, otherwise volatile species may be lost. Naturally, care is necessary to avoid contamination. The use of microwave-assisted heating is the better way to perform acid mineralization. Sample dilution is evidently very attractive, due to its simplicity. However, this simplicity must not lead the analyst to forget that oil is a very complex mixture, and its composition changes according to its origin. Complete solubilization may be difficult, due to the presence of water clusters that may contain inorganic salts. Furthermore, not all organic compounds are soluble in the more common organic solvents that are appropriate to the subsequent atomic spectrometric measurement. In some cases, an appropriate solvent mixture, with solvents of different polarities, may be the best choice. In the case of ICP techniques, more frequent replacement of spectrometer consumables (sampler, skimmer, torches, injectors) due to the higher corrosion caused by an oxygen–argon plasma is necessary. ICP-MS requires periodic lens cleaning due to carbon build-up. The direct solvent introduction technique is limited by the availability of organometallic standards and calibration problems as well as the stability of the sample (after dilution) and analytical solutions at the μg $\text{L}^{-1}$ level, which must be addressed. However, it is a fast methodology, less prone to contamination and losses, and gives better precision than decomposition procedures. In fact, for comparative results, the instrumental conditions must be strictly known, for ICP as well as for flame techniques. In the case of ET AAS, the presence of volatile compounds that are lost during the pyrolysis step is well demonstrated. Their stabilization must be considered, and the use of an appropriate modifier, even for elements known as non-volatile, is necessary. Proper emulsion formation techniques produce systems stable enough for a practical atomic spectrometric determination and are promising for elements difficult to stabilize and to determine by decomposition or solvent dilution procedures. However, they are more time-consuming and less reproducible than solvent solubilization procedures. Results derived from emulsion methods correspond to total element content, whereas those based on the solubilization by aromatic or aliphatic solvents allow the determination of elements associated only with the organic phase. The applicability of direct "solid" sampling of oil samples has been demonstrated for few elements using ET AAS. In this case, as well as in the previous ones, STPF conditions must be closely followed, together with the use of an efficient background correction system. In this sense, CS–ET AAS will certainly open new possibilities. Direct sampling procedures may also be easily adapted to ETV–ICP-MS. Polyatomic interferences in quadrupole ICP-MS must also be considered. For instance, the matrix interference on Cr does not seem to be resolved by any methodology, since residual carbon is always present, and only the use of DRC/CC- or HR-ICP-MS can overcome this problem. These limitations lead, once again, to the necessity of improvements in sample preparation steps. The early method of extraction of water-soluble salts from the crude oils, often neglected in the past, is recommended for generating reliable results on trace element concentrations in the organic phase. The determination of trace elements in operationally defined fractions of crude oil is another step forward for its better characterization, allowing new geochemical applications. Following the general trend in analytical chemistry, metal speciation will also have its important place in oil analysis, specifically for less explored fractions, such as resin and asphaltenes.

## 4. List of acronyms

| | |
|---|---|
| AFS | Atomic fluorescence spectrometry |
| ASTM | American Society for Testing Materials |
| BTX | Benzene, toluene and xylene |
| CC | Collision cell |
| CV | Cold vapor |
| CVG | Chemical vapor generator |
| DIN | Direct injection nebulizers |
| DIHEN | Direct injection high efficiency nebulizer |
| DRC | Dynamic reaction cell |
| ET AAS | Electrothermal atomic absorption spectrometry |
| ETV | Electrothermal vaporization |
| FAAS | Flame atomic spectrometry |
| GC | Gas chromatography |
| HG AAS | Hydride generation atomic absorption spectrometry |
| HPLC | High performance liquid chromatography |
| HR-ICP-MS | High resolution inductively coupled plasma mass spectrometry |
| ICP-MS | Inductively coupled plasma mass spectrometry |
| ICP OES | Inductively coupled plasma optical emission spectrometry |
| ICP-TOF-MS | Inductively coupled plasma time-of-flight mass spectrometry |
| NdYAG | Neodymium-doped yttrium aluminum garnet |
| o/w | oil-in-water emulsion |
| SARA | Saturated, aromatic, resin and asphaltene fractions |
| SPL | Solvent plasma load |
| SRM | Standard reference material |
| STPF | Stabilized temperature platform furnace |
| THGF | Transversely heated graphite furnace |
| w/o | water-in-oil emulsion |

## Acknowledgements

The authors thank CNPq (Brazil) for scholarships and Petrobras for research funding.

## References

[1] B.P. Tissot, D.H. Welte, Petroleum Formation and Occurrence, 1st ed. Springer-Verlag, Berlin, 1984.

[2] A. Treibs, Chlorophyll-und Häminderivate in bituminösen Gesteinen, Erdölen, Erdwachsen und Asphalten, Liebigs Ann. Chem. 510 (1934) 42–62.

[3] E.A. Glebovskaya, M.V. Volkenshtein, Spektry porfirinov V neftyakh i bitumakh, Zh. Obshch. Khim. (USSR) 18 (1948) 1440–1451.

[4] T.F. Yen, The Role of Trace Metals in Petroleum, Ann Harbor Science Publishers Inc., Michigan, 1975.

[5] J.S. Ball, W.J. Wenger, H.J. Hyden, C.A. Horr, A.T. Myers, Metal content of twenty-four petroleums, J. Chem. Eng. Data 5 (1960) 553–557.

[6] H. Al-Shahristani, M.J. Al-Atyia, Vertical migration of oil in Iraqi oil fields: Evidence based on vanadium and nickel concentrations, Geochim. Cosmochim. Acta 36 (1972) 929–938.

[7] M. El-Gayar, M.S. Mostafa, A.E. Abdelfattah, A.O. Barakat, Application of geochemical parameters for classification of crude oils from Egypt into source-related types, Fuel Process. Technol. 79 (2002) 13–28.

[8] M.D. Lewan, J.B. Maynard, Factors controlling enrichment of vanadium and nickel in the bitumen of organic sedimentary rocks, Geochim. Cosmochim. Acta 46 (1982) 2547–2560.

[9] M.D. Lewan, Factors controlling the proportionality of vanadium to nickel in crude oils, Geochim. Cosmochim. Acta 48 (1984) 2231–2238.

[10] B.M. Didyk, Y.I.A. Alturki, C.T. Pillinger, G. Eglington, Petroporphyrins as indicators of geothermal maturation, Nature 256 (1975) 563–565.

[11] A.J.G. Barwise, Mechanisms involved in altering deoxophylloerythroetioporphyrin–etioporphyrin ratios in sediments and oils, J. Am. Chem. Soc. Spec. Pub. 344 (1987) 100–109.

[12] K.E. Peters, C.C. Walters, J.M. Moldowan, 2nd ed., The Biomarker Guide, Volume 2: Biomarkers and Isotopes in the Petroleum Exploration and Earth History, Cambridge University Press, New York, 2004.

[13] E. Les Ebdon, H. Evans, W.G. Pretorius, S.J. Rowland, Analysis of geoporphyrins by high-temperature gas chromatography inductively coupled plasma mass spectrometry and high-performance liquid chromatography inductively coupled plasma mass spectrometry, J. Anal. At. Spectrom. 9 (1994) 939–943.

[14] C. Schickling, J. Broeckaert, Determination of mercury species in gas-condensates by online coupled high-performance liquid-chromatography and cold-vapor atomic absorption spectrometry, Appl. Organomet. Chem. 9 (1985) 29–36.

[15] H. Tao, T. Murakami, M. Tominaga, A. Miyazaki, Mercury speciation in natural gas condensate by gas chromatography-inductively coupled plasma mass spectrometry, J. Anal. At. Spectrom. 13 (1998) 1085–1093.

[16] J. Ellrich, A. Hirner, H. Stärk, Distribution of trace elements in crude oils from southern Germany, Chem. Geol. 48 (1985) 313–323.

[17] M. Alberdi-Grenolet, R. Tocco, Trace metals and organic geochemistry of the Machiques Member (Aptian–Albian) and La Luna Formation (Cenomanian–Campanian), Venezuela, Chem. Geol. 160 (1999) 19–38.

[18] T.C.O. Fonseca, PhD Thesis, Chemistry Department, PUC-RJ, Brazil, (2000), 135 pp.

[19] J.A. Curiale, Distribution and occurrence of metals in heavy crude oils and betumens, AAPG Stud. Geol. 25 (1987) 207–219.

[20] S.D. Olsen, R.H. Filby, T. Brekket, G.H. Isaksen, Analysis of metals in condensates and naphta by inductively coupled plasma mass spectrometry, Analyst 120 (1995) 1379–1390.

[21] B. Hitchon, E.H. Perkins, W.D. Gunter, Recovery of trace metals in formation waters using acid gases from natural gas, Appl. Geochem. 16 (2001) 1481–1497.

[22] R.H. Filby, Origin and nature of trace element species in crude oil, bitumens and kerogens: implications for correlation and other geochemical studies, Geol. Soc. Spec. Pub. 78 (1994) 203–219.

[23] H.G. Machel, Bacterial and thermochemical sulfate reduction in diagenetic settings — old and new insights, Sediment. Geol. 140 (2001) 143–175.

[24] IP 143: Determination of asphaltenes (heptane insolubles) in crude petroleum and petroleum products, Energy institute (former Institute of Petroleum), 2004, ref: 978 0 85293.

[25] ASTM D, Standard Test Method for Characteristic Groups in Rubber Extender and Processing Oils and Other Petroleum-Derived Oils by the Clay–Gel Absorption Chromatographic Method, 2007, pp. 1–8.

[26] J.G. Speight, in: John Wiley (Ed.), Handbook of Petroleum Product Analysis (Chemical Analysis: A Series of Monographs on Analytical Chemistry and Its Applications), Wiley-Interscience, 2001, pp. 245–259.

[27] J.G. Speight, New approaches to hydroprocessing, Catal. Today 98 (2004) 55–60.

[28] L. Lopez, S. Ló Monaco, Geochemical implications of trace elements and sulfur in the saturate, aromatic and resin fractions of crude oil from the Mara and Mara Oeste fields, Venezuela, Fuel 83 (2004) 365–374.

[29] S. Ló Monaco, L. Lopez, G. Garban, A. Lira, A. Rojas, Determinación de elementos traza en kerogeno, bitumen y fracciones del petróleo, utilizando espectrometría de plasma (ICP), Rev. Lat.-Am. Geoquim. Org. 3 (1997) 43–54.

[30] C. Duyck, PhD Thesis, Chemistry Department, PUC-RJ, Brazil, (2001), 203p.

[31] C. Duyck, N. Miekeley, C.L.P. Silveira, P. Szatmari, Trace element determination in crude oil and its fractions by inductively coupled plasma mass spectrometry using ultrasonic nebulization of toluene solutions, Spectrochim. Acta 57B (2002) 1979–1990.

[32] S.M. Wilhelms, L. Liang, D. Kirchgessner, Identification and properties of mercury species in crude oil, Energy Fuels 20 (2006) 180–186.

[33] T.F. Yen, G.V. Chiligarian (Eds.), Asphaltenes and Asphalts, 1st. ed., Developments in Petroleum Science, vol. 1, Elsevier, New York, 2000.

[34] M. El-Gayar, Aromatic steroids in Mideastern crude oils: identification and geochemical application, Pet. Sci. Technol. 21 (2003) 719–726.

[35] T.J. Kaminski, H.S. Fogler, N. Wolf, P. Wattana, A. Mairal, Classification of asphaltenes via fractionation and the effect of heteroatom content on dissolution kinetics, Energy Fuels 14 (2000) 25–30.

[36] J.G. Gary, G.E. Handwerk, Chemical Processing and Engineering, 4th. ed.Marcel Dekker Inc., New York, 2001.

[37] N. Panariti, A. Del Bianco, G. Del Piero, M. Marchionna, Petroleum residue upgrading with dispersed catalysts. Part 1. Catalysts activity and selectivity, Appl. Catal. 204A (2000) 203–213.

[38] K.H. Altgelt, M.M. Boduszynski, Composition and Analysis of Heavy Petroleum Fractions (Chemical Industries), 1st. ed.Marcel Dekker Inc., New York, 1994.

[39] J.G. Speight, Petroleum asphaltenes — Part 1 — asphaltenes, resins and the structure of petroleum, Oil Gas Sci. Technol.-Rev. IFP 59 (2004) 467–477.

[40] J.G. Reynolds, Nickel in petroleum refining, Pet. Sci. Technol. 19 (2001) 979–1007.

[41] E. Furimsky, Selection of catalysts and reactors for hydroprocessing, Appl. Catal. 171A (1998) 177–206.

[42] M.S. Rana, M.S. Ancheyta, J. Maity, S.K., P. Rayo, Comparative study for heavy oil hydroprocessing catalysts at micro-flow and bench-scale reactors, Catal. Today 109 (2005) 61–68.

[43] J.P. Dunn, H.G. Stenger, I.E. Wachs, Molecular structure-reactivity relationships for the oxidation of sulfur dioxide over supported metal oxide catalysts, Catal. Today 53 (1999) 543–556.

[44] A. Samecka-Cymerman, K. Kolon, A.J. Kempers, Differences in concentration of heavy metals between native and transplanted Plagiothecium denticulatum: a case study of soils contaminated by oil well exudates in South East Poland, Arch. Environ. Contam. Toxicol. 49 (2005) 317–321.

[45] L.C. Osuji, S.O. Adesiyan, Extractable hydrocarbons, nickel and vanadium contents of Ogbodo–Isiokpo oil spill polluted soils in Niger Delta, Nigeria, Environ. Monit. Assess. 110 (2005) 129–139.

[46] M.P. Pavageau, A. Mirin, F. Seby, C. Guimon, E. Krupp, C. Pécheyran, J. Poulleau, O.F.X. Donard, Partitioning of metal species during an enriched fuel combustion experiment. Speciation in the gaseous and particulate phases, Environ. Sci. Technol. 38 (2004) 2252–2263.

[47] H.Y.N. Holeman, R. Goth-Goldenstein, D. Aston, M. Yun, J. Kengsoontra, Evaluation of gastrointestinal solubilization of petroleum hydrocarbon residues in soil using an in vitro physiologically based model, Environ. Sci. Technol. 36 (2002) 1281–1286.

[48] M.F. Soto-Jimenez, S.A. Hibdon, C.W. Rankin, J. Aggarawl, A.C. Ruiz-Fernandez, F. Paez-Osuna, A.R. Flegal, Chronicling a century of lead pollution in Mexico: stable lead isotopic composition analyses of dated sediment cores, Environ. Sci. Technol. 40 (2006) 764–770.

[49] W. Kovarik, Ethyl-leaded gasoline: how a classic occupational disease became an international public health disaster, Int. J. Occup. Environ. Health 11 (2005) 384–397.

[50] X.G. Meng, S. Bang, G.P. Korfiatis, Removal of selenocyanate from water using elemental iron, Water Res. 36 (2002) 3867–3873.

[51] N. Miekeley, R.C. Pereira, E.A. Casartelli, A.C. Almeida, M.F.B. Carvalho, Inorganic speciation analysis of selenium by ion chromatography-inductively coupled plasma-mass spectrometry and its application to effluents from a petroleum refinery, Spectrochim. Acta 60B (2005) 633–641.

[52] C.P. Lienemann, Analyse de métaux traces dans les produits pétroliers, état de l'art, Oil Gas Sci. Technol.- Rev. IFP 60 (6) (2005) 951–965.

[53] R.W. Kelly, S.E. Long, J.L. Mann, Determination of mercury in SRM crude oils and refined products by isotope dilution cold vapor ICP-MS using closed-system combustion, Anal. Bioanal. Chem. 376 (2003) 753–758.

[54] Z. Kowalewska, A. Ruszczynska, E. Bulska, Cu determination in crude oil distillation products by atomic absorption and inductively coupled plasma mass spectrometry after analyte transfer to aqueous solution, Spectrochim. Acta 60B (2005) 351–359.

[55] A. Montaser (Ed.), Inductively Coupled Plasma Mass Spectrometry, 1st.ed., Wiley-VCH, New York, 1998.

[56] C.J. Lord, Determination of trace metals in crude oil by inductively coupled plasma mass spectrometry with micro-emulsion sample introduction, Anal. Chem. 63 (1991) 1594–1599.

[57] A.W. Boorn, R.F. Browner, Effects of organic solvents in inductively coupled plasma atomic emission spectrometry, Anal. Chem. 54 (1992) 1402–1410.

[58] R.I. Botto, J. Zhu, Use of an ultrasonic nebulizer with membrane desolvation for analysis of volatile solvents by inductively coupled plasma atomic emission spectrometry, J. Anal. At. Spectrom. 9 (1994) 905–912.

[59] I.B. Brenner, A. Zander, M. Plantz, J. Zhu, Characterization of an ultrasonic nebulizer-membrane separation interface with inductively coupled plasma mass spectrometry for the determination of trace elements by solvent extraction, J. Anal. At. Spectrom. 12 (1997) 273–279.

[60] T.D. Saint'Pierre, L.F. Dias, D. Pozebon, R.Q. Aucélio, A.J. Curtius, B. Welz, Determination of Cu, Mn, Ni and Sn in gasoline by ETV–ICP-MS and emulsion sample introduction, Spectrochim. Acta 57B (2002) 1991–2001.

[61] F.J.M.J. Maessen, P.J.H. Seeverens, G. Kreuning, Analytical aspects of organic solvent load reduction in normal-power ICPs by aerosol thermostating at low temperatures, Spectrochim. Acta 39B (1984) 1171–1180.

[62] D. Hausler, Trace element analysis of organic solutions using inductively coupled plasma-mass spectrometry, Spectrochim. Acta 42B (1987) 63–73.

[63] J. Sneddon, C. Hardaway, K.K. Bobbadi, J.N. Beck, A study of a crude oil spill site for selected metal concentrations remediated by a controlled burning in Southwest Louisiana, Microchem. J. 82 (2006) 8–16.

[64] B. Welz, H. Becker-Ross, S. Florek, U. Heitman, High-resolution Continuum Source AAS: The Better Way to do Atomic Absorption Spectrometry, 1st. ed.Wiley-VCH, Weinheim, 2005.

[65] R.C. Campos, M.C.R. Resende, A.J. Curtius, Application of the cold vapor technique to the speciation of mercury in fish samples after solvent

extraction and methylmercury reduction directly in the organic medium, J. Anal. At. Spectrom. 8 (1993) 247–251.

[66] R.C. Campos, G.P. Brandão, A.S. Luna, Determination of mercury in gasoline by cold vapor atomic absorption spectrometry with direct reduction in micro-emulsion media, Spectrochim. Acta 60B (2005) 625–631.

[67] M. Murillo, N. Carrión, J. Chirinos, Determination of sulphur in crude oils and related materials with a Parr bomb digestion method and inductively coupled plasma atomic emission spectrometry, J. Anal. At. Spectrom. 8 (1993) 493–495.

[68] A.L.M. Bastos, M.Sc. Thesis, Chemistry Department, PUC-RJ, Brazil, (2005).

[69] F.E. Smith, E.A. Arsenault, Microwave-assisted sample preparation in analytical chemistry, Talanta 43 (1996) 1207–1268.

[70] V.F. Taylor, A. Toms, H.P. Longerich, Acid digestion of geological and environmental samples using open-vessel focused microwave digestion, Anal. Bioanal. Chem. 372 (2002) 360–365.

[71] L.M. Costa, F.V. Silva, S.T. Gouveia, A.R.A. Nogueira, J.A. Nóbrega, Focused microwave-assisted acid digestion of oils: an evaluation of the residual carbon content, Spectrochim. Acta 56B (2001) 1981–1985.

[72] T. Wondimu, W. Goessler, K.J. Irgolic, Microwave digestion of residual fuel oil for the determination of trace elements by inductively coupled plasma mass spectrometry, Fresenius' J. Anal. Chem. 367 (2000) 35–42.

[73] T. Wondimu, W. Goessler, Comparison of closed-pressurized and open-refluxed vessel digestion systems for trace elements in the residual fuel oil reference material (SRM 1634c), Bull. Chem. Soc. Ethiop. 14 (2000) 99–113.

[74] N. Jakubowski, J. Feldmann, D. Stuewer, Analytical improvement of pneumatic nebulization in ICP-MS by desolvation, Spectrochim. Acta 47B (1992) 107–118.

[75] S.H. Tan, G. Horlick, Background spectral features in inductively coupled plasma/mass spectrometry, Appl. Spectrosc. 40 (1986) 445–460.

[76] V.N. Epov, D. Lariviere, E.N. Epova, R.D. Evans, Polyatomic interferences produced by macro elements during direct multi-elemental ICP-MS hydrochemical analysis, Geostand. Geoanal. Res. 28 (2004) 213–224.

[77] D.W. Koppenaal, G.C. Eiden, C.J. Barinaga, Collision and reaction cells in atomic mass spectrometry: development, status, and applications, J. Anal. At. Spectrom. 19 (2004) 561–570.

[78] A.P. Udoh, S.A. Thomas, E.J. Ekanem, Application of *p*-xylenesulphonic acid as ashing reagent in the determination of trace metals in crude oil, Talanta 39 (1992) 1591–1595.

[79] O. Platteau, M. Carrillo, Determination of metallic elements in crude oil–water emulsions by flame AAS, Fuel 74 (1995) 74–76.

[80] Standard test methods for determination of nickel, vanadium, iron, and sodium in crude oils and residual fuels by flame atomic absorption spectrometry ASTM D5863-00a (2005).

[81] S.H. Kagler, R. Kotzel, Die Bestimmung von Cd im Bereich < 10 μg/kg in Mineralölprodukten mittels Graphitrohrofen, Fortschritte in der atomspektrometrischen Spurenanalytik, Band, vol. 1, Verlag Chemie, Berlin, 1984.

[82] V. Sychra, I. Lang, G. Sebor, Analysis of petroleum and petroleum products by atomic absorption spectroscopy and related techniques: Crude oils. Heavy petroleum oils and residues, Prog. Anal. At. Spectrom. 4 (1981) 349–372.

[83] Standard test methods for determination of aluminum and silicon in fuel oils by ashing, fusion, inductively coupled plasma atomic emission spectrometry, and atomic absorption spectrometry, ASTM D5184-01 (2006).

[84] Acid digestion of oils for metals analysis by atomic absorption or ICP spectrometry, US-EPA Method 3031 (1996).

[85] H.P.M. Stigter, R. de Haan, C.P.A. Guicherit, M.L. Dekkers, Determination of cadmium, zinc, copper, chromium and arsenic I crude oil cargoes, Environ. Pollut. 107 (2000) 451–464.

[86] M. Turunen, S. Peraniemi, M. Ahlgrén, H. Westerholm, Determination of trace elements in heavy oil samples by graphite furnace and cold vapor atomic absorption spectrometry after acid digestion, Anal. Chim. Acta 311 (1995) 85–91.

[87] Microwave assisted acid digestion of sediments, sludges, soils and oils, US-EPA 3051 (1994).

[88] J. Alvarado, A.R. Picon, C.M. de Vecchi, Microwave wet acid digestion in the preparation of crude oil samples for AAS determination of their chromium, copper, iron, manganese, sodium, nickel, vanadium and zinc content, Acta Chim. Ven. 41 (1990) 306–319.

[89] M. Bettinelli, S. Spezia, U. Baroni, G. Bizzarri, Determination of trace elements in fuel oils by inductively coupled plasma mass spectrometry after acid mineralization of sample in microwave oven, J. Anal. At. Spectrom. 10 (1995) 555–560.

[90] M. Krachler, H. Radner, K.J. Irgolic, Microwave digestion methods for the determination of trace elements in brain and liver samples by inductively coupled plasma mass spectrometry, Fresenius' J. Anal. Chem. 355 (1996) 120–128.

[91] M.B. Campbell, G.A. Kanert, High-pressure microwave digestion for the determination of arsenic, antimony, selenium and mercury in oily wastes, Analyst 117 (1992) 121–124.

[92] B.K. Puri, K.J. Irgolic, Determination of arsenic in crude petroleum and liquid hydrocarbons, Environ. Geochem. Health 11 (1989) 95–99.

[93] Z.C. Hu, S. Gao, S.H. Hu, H.L. Yuan, X.M. Liua, Y.S. Liu, Suppression of interferences for direct determination of arsenic in geological samples by inductively coupled plasma mass spectrometry, J. Anal. At. Spectrom. 20 (2005) 1263–1269.

[94] B. Welz, M. Melcher, Mechanisms of transition metal interferences in hydride generation atomic absorption spectrometry. Part 3. Releasing effect of iron(III) on nickel interference on arsenic and selenium, Analyst 109 (1984) 577–579.

[95] G. Bagur, D. Gazquez, M. Sanches, A.M. Martin, Synergistic extraction atomic spectrophotometric determination of vanadium in foods and petroleum crudes with 5,5′-methylenedisalicylohydroxamic acid (medsha), Anal. Lett. 26 (1993) 125–140.

[96] R.I. Botto, Applications of ultrasonic nebulization in the analysis of petroleum and petrochemicals by inductively coupled plasma atomic emission spectrometry, J. Anal. At. Spectrom. 8 (1993) 51–57.

[97] R.I. Botto, J. Zhu, Universal calibration for analysis of organic solutions by inductively coupled plasma atomic emission spectrometry, J. Anal. At. Spectrom. 11 (1996) 675–681.

[98] R.I. Botto, Trace element analysis of petroleum naphtas and tars using direct injection ICP-MS, Can. J. Anal. Sci. Spectrosc. 47 (2002) 1–13.

[99] R.C. Hutton, Application of inductively coupled plasma source mass spectrometry (ICP-MS) to the determination of trace metals in organics, J. Anal. At. Spectrom. 1 (1986) 259–263.

[100] B. Magyar, P. Lienemann, H. Vonmont, Some effects of aerosol drying and oxygen feeding on the analytical performance of an inductively coupled nitrogen–argon plasma, Spectrochim. Acta 41B (1986) 27–38.

[101] G.R. Peters, D. Beauchemin, Characterization of an interface allowing either nebulization or gas chromatography as the sample introduction system in ICP-MS, Anal. Chem. 65 (1993) 97–103.

[102] L.C. Alves, M.G. Minnich, D.R. Wiederin, R.S. Houk, Removal of organic solvents by cryogenic desolvation in inductively coupled plasma mass spectrometry, J. Anal. At. Spectrom. 9 (1994) 399–403.

[103] I.B. Brenner, J. Zhu, A. Zander, Evaluation of an ultrasonic nebulizer-membrane separation interface (USN-MEMSEP) with ICP-AES for the determination of trace elements by solvent, Fresenius' J. Anal. Chem. 335 (1996) 774–777.

[104] S.D. Olsen, S. Westerlund, R.G. Visser, Analysis of metals and condensates in naphta by inductively coupled plasma mass spectrometry, Analyst 122 (1997) 1229–1234.

[105] K. Kahen, A. Strubinger, J.R. Chirinos, A. Montaser, Direct injection high efficiency nebulizer-inductively coupled plasma mass spectrometry for analysis of petroleum samples, Spectrochim. Acta 58B (2003) 397–413.

[106] E. Björn, W. Frech, Introduction of high carbon content solvents into inductively coupled plasma mass spectrometry by a direct injection high efficiency nebuliser, Anal. Bioanal. Chem. 376 (2003) 274–278.

[107] S.E. Maestre, J.L. Todoli, J.M. Mermet, Evaluation of several pneumatic micronebulizers with different designs for use in ICP-AES and ICP-MS. Future directions for further improvement, Anal. Bioanal. Chem. 379 (2004) 888–899.

[108] S. Dreyfus, C. Pécheyran, C. Magnier, A. Prinzhofer, C.P. Lienemann, O. F.X. Donard, Direct trace and ultra-trace metals determination in crude oil and fractions by inductively coupled plasma mass spectrometry, ASTM J. 2 (2005) 1–8.

[109] S.J. Kumat, S. Gangadharan, Determination of trace elements in naphta by inductively coupled plasma mass spectrometry using water-in-oil emulsions, J. Anal. At. Spectrom. 14 (1999) 967–971.

[110] M. Murillo, J. Chirinos, Use of emulsion systems for the determination of sulfur, nickel and vanadium in heavy crude oil samples by inductively coupled plasma atomic emission spectrometry, J. Anal. At. Spectrom. 9 (1994) 237–240.

[111] M. Murillo, J. Chirinos, Study of the effect of organic emulsified samples in inductively coupled plasma atomic emission spectrometry, J. Anal. At. Spectrom. 11 (1996) 253–257.

[112] R.M. Souza, A.L.S., C.L.P. da Silveira, R.Q., Determination of Mo, Zn, Cd, Ti, Ni, V Fe, Mn, Cr and Co in crude oil using inductively coupled plasma optical emission spectrometry and sample introduction as detergentless micro-emulsions, Microchem. J. 82 (2006) 137–141.

[113] T. Greibrokk, E. Lundanes, H.R. Norli, K. Dyrstad, S.D. Olsen, Experimental simulation of oil migration–distribution effects on organic compound groups and on metal/metal ratios, Chem. Geol. 116 (1994) 281–299.

[114] N.H. Bings, Direct determination of metals in lubricating oils by laser ablation coupled to inductively coupled plasma time-of-flight mass spectrometry, J. Anal. At. Spectrom. 17 (2002) 759–767.

[115] J.L. Fabec, M.L. Ruschak, Determination of nickel, vanadium, and sulfur in crudes and heavy crude fractions by inductively coupled argon plasma/atomic emission spectrometry and flame atomic absorption spectrometry, Anal. Chem. 57 (1985) 1853–1863.

[116] J.M. Guidr, J. Sneddon, Fate of vanadium determined by nitrous oxide–acetylene flame atomic absorption spectrometry in unburned and burned Venezuelan crude oil, Microchem. J. 73 (2002) 363–366.

[117] J.L. Hammond, Y. Lee, C.O. Noble, J.N. Beck, C.E. Proffitt, J. Sneddon, Determination of cadmium, lead, and nickel by simultaneous multielement flame atomic absorption spectrometry in burned and unburned Venezuelan crude oil, Talanta 47 (1998) 261–266.

[118] O. Osibanjo, S.E. Kakulu, S.O. Ajayi, Analytical application of inorganic salt standards and mixed-solvent systems to trace-metal determination in petroleum crudes by atomic absorption spectrophotometry, Analyst 109 (1984) 109–127.

[119] Sebor, G.I. Lang, D. Kolihova, O. Wasser, Effect of the type of organometallic iron and copper compounds on the determination of both metals in petroleum samples by flame atomic-absorption spectroscopy, Analyst 107 (1982) 1350–1355.

[120] M. Bettinelli, P. Tittarelli, Evaluation and validation of instrumental procedures for the determination of nickel and vanadium in fuel oils, J. Anal. At. Spectrom. 9 (1994) 805–812.

[121] C.F. Bruhn, V.G. Cabalín, Direct determination of nickel in gas oil by atomic absorption spectrometry with electrothermal atomization, Anal. Chim. Acta 143 (1983) 193–203.

[122] M.C. González, A.R. Rodriguez, V. González, Determination of vanadium, nickel, iron, copper, and lead in petroleum fractions by atomic absorption spectrophotometry with a graphite furnace, Microchem. J. 57 (1987) 94–106.

[123] P. Bermejo-Barrera, C. Pita-Calvo, F. Bermejo-Marinez, Simple preparation procedures for vanadium determination in petroleum by atomic-absorption spectrometry with electrothermal atomization, Anal. Lett. 24 (1991) 447–458.

[124] N.S. Thomaidis, E.A. Piperaki, Comparison of chemical modifiers for the determination of vanadium in water and oil samples by electrothermal atomization atomic absorption spectrometry, Analyst 121 (1996) 111–117.

[125] Y. Nakamoto, T. Ishimaru, N. Endo, K. Matsusaki, Determination of vanadium in heavy oils by atomic absorption spectrometry using graphite furnace coated with tungsten, Anal. Sci. 20 (2004) 739–741.

[126] M. de la Guardia, M.J. Lizondo, Direct determination of nickel in fuel oil by atomic absorption spectrometry using emulsions, At. Spectr. 6 (1993) 208–211.

[127] N.N. Meeravali, S.J. Kumar, The utility of a W–Ir permanent chemical modifier for the determination of Ni and V in emulsified fuel oils and naphtha by transverse heated electrothermal atomic absorption spectrometer, J. Anal. At. Spectrom. 16 (2001) 527–532.

[128] J.L. Burguera, R.M. Avila-Gomez, M. Burguera, R.A. de Salaguer, J.L. Salaguer, C.L. Bracho, M. Burguera-Pascu, C. Burguera-Pascu, R. Brunetto, M. Gallignani, Y.P. de Pena, Optimum phase-behavior formulation of surfactant/oil/water systems for the determination of chromium in heavy crude oil and in bitumen-in-water emulsion, Talanta 61 (2003) 353–361.

[129] M.G.R. Vale, I.C.F. Damin, A. Klassen, M.M. Silva, B. Welz, A.F. Silva, F.G. Lepri, D.L.G. Borges, U. Heitmann, Method development for the determination of nickel in petroleum using line-source and high-resolution continuum-source graphite furnace atomic absorption spectrometry, Microchem. J. 77 (2004) 131–140.

[130] R.Q. Aucelio, A. Doyle, B.S. Pizzorno, M.L.B. Tristão, R.C. Campos, Electrothermal atomic absorption apectrometric method for the determination of vanadium in diesel and asphaltene prepared as detergentless microemulsions, Microchem. J. 78 (2004) 21–26.

[131] I.C.F. Damin, M.G.R. Vale, M.M. Silva, B. Welz, F.G. Lepri, W.N.L. Santos, S.L.C. Ferreira, Palladium as chemical modifier for the stabilization of volatile nickel and vanadium compounds in crude oil using graphite furnace atomic absorption spectrometry, J. Anal. At. Spectrom. 20 (2005) 1332–1336.

[132] M.N.M. Reyes, R.C. Campos, Determination of copper and nickel in vegetable oils by direct sampling graphite furnace atomic absorption spectrometry, Talanta 70 (2006) 929–932.

[133] G.P. Brandão, R.C. Campos, E.V.R. de Castro, H.C. de Jesus, Direct determination of nickel in petroleum by solid sampling-graphite furnace atomic absorption spectrometry, Anal. Bioanal. Chem. 386 (2006) 2249–2253.

[134] M.M. Silva, I.C.F. Damin, M.G.R. Vale, B. Welz, Feasibility of using solid sampling graphite furnace atomic absorption spectrometry for speciation analysis of volatile and non-volatile compounds of nickel and vanadium in crude oil, Talanta 71 (2007) 349–359.

[135] G.P. Brandão, R.C. de Campos, E.V.R. de Castro, H.C. de Jesus, Direct determination of copper, iron and vanadium in petroleum by solid sampling-graphite furnace atomic absorption spectrometry, Spectrochim. Acta Part B 62 (2007) 962–969 (this issue), doi:10.1016/j.sab.2007.05.001.

[136] R.H. Fish, J.J. Komlenic, Molecular characterization and profile identifications of vanadyl compounds in heavy crude petroleums by liquid chromatography/graphite furnace atomic absorption spectrometry, Anal. Chem. 56 (1984) 510–517.

[137] R.H. Fish, J.J. Komlenic, B.K. Wines, Characterization and comparison of vanadyl and nickel compounds in heavy crude petroleums and asphaltenes by reverse-phase and size-exclusion liquid chromatography/graphite furnace atomic absorption spectrometry, Anal. Chem. 56 (1984) 2452–2460.

[138] N. Marqueza, F. Ysambertta, C. De La Cruz, Three analytical methods to isolate and characterize vanadium and nickel porphyrins from heavy crude oil, Anal. Chim. Acta 395 (1999) 343–349.

[139] F.G. Lepri, B. Welz, D.L.G. Borges, A.F. Silva, M.G.R. Vale, U. Heitmann, Speciation analysis of volatile and non-volatile vanadium compounds in Brazilian crude oils using high-resolution continuum source graphite furnace atomic absorption spectrometry, Anal. Chim. Acta 558 (2006) 195–200.

[140] U. Kumar, J.G. Dorsey, J.A. Caruso, Metalloporphyrin speciation by liquid chromatography and inductively coupled plasma mass spectrometry, J. Chromatogr. Sci. 32 (1994) 282–285.

[141] K.L. Ackley, J.A. Day, J.A. Caruso, Separation of metalloporphyrins by capillary electrophoresis with UV detection and inductively coupled plasma mass spectrometric detection, J. Chromatogr., A 888 (2005) 293–298.

Anal Bioanal Chem (2006) 386:2249–2253
DOI 10.1007/s00216-006-0875-6

TECHNICAL NOTE

# Direct determination of nickel in petroleum by solid sampling–graphite furnace atomic absorption spectrometry

**Geisamanda Pedrini Brandão** ·
**Reinaldo Calixto de Campos** ·
**Eustáquio Vinicius Ribeiro de Castro** ·
**Honério Coutinho de Jesus**

Received: 4 June 2006 /Revised: 4 September 2006 /Accepted: 21 September 2006 / Published online: 24 October 2006

**Abstract** A procedure for the direct GFAAS determination of Ni in petroleum samples using a solid sampling strategy is proposed. Palladium was used as conventional modifier. Central composite design multivariate optimization defined the optimum temperature program and the Pd mass, allowing calibration using aqueous analytical solution. The limit of detection (LOD) at the optimized conditions was 0.23 ng of Ni, for typical sample masses between of 0.10 and 0.60 mg. Linearity at least up to 11 ng of Ni and a characteristic mass of 45 pg were observed, defining a dynamic range between 0.52 and 110 µg $g^{-1}$. Typical coefficients of variation ($n=10$) in the analysis of oil reference materials were 7%. Method validation was performed both by the analysis of oil certified reference materials and by comparison with an independent method (ASTM 5863-B). No statistically significant difference was observed between obtained and expected values. The total determination cycle lasted 5 min, equivalent to a sample throughput of 6 $h^{-1}$ for duplicate determinations.

**Keywords** Nickel · Petroleum · SS-GFAAS

## Introduction

The determination of metallic trace elements in petroleum is of importance to the oil industry, since it provides information about crude oil origins, migration, and types. Nickel naturally occurs in petroleum at the µg $g^{-1}$ range associated to the formation process, mostly as metalloporphyrins and metallonon-porphyrins [1–3]. Ni interferes with the refining of crude oils: it may cause corrosion of refinery equipment and affects catalyst activity, leading to undesirable side reactions and decreasing cracking yields [3, 4]. Hazardous Ni compounds might also be generated during combustion of petroleum and its derivatives, leading to environmental and health concerns. Consequently, Ni emissions control under national and international regulations have been established. The evaluation of the Ni concentration may also be utilized to identify sources of unregulated releases of petroleum [4, 5]. A number of analytical methods for the determination of Ni in petroleum and their viscous heavy products have been proposed including X-ray fluorescence spectroscopy [6–8], high-performance liquid chromatographic (HPLC) with UV [9] or atomic absorption spectrometry (AAS) [1] detection, inductively coupled plasma optical emission (ICPOES) [4, 10–12] and mass spectrometry (ICPMS) [13–16], flame atomic absorption spectrometry (FAAS) [2, 5, 17–19], and graphite furnace atomic absorption spectrometry (GFAAS) [20–23]. In ICP techniques desolvatation under cryogenic cooling and the removal of carbon by feeding oxygen into the plasma [16] have been proposed in order to avoid plasma extinction or carbon deposition on the sampler and skimmer cones. FAAS allows the direct analysis of hydrocarbon matrices after just a dilution with an adequate organic solvent. However, aside from its low sensitivity, both the solvent and the compounds used for calibration

G. P. Brandão · R. C. de Campos (✉)
Department of Chemistry, Pontifical Catholic University,
Rua Marquês de S. Vicente 225,
Gávea 22453-900 RJ, Brazil
e-mail: rccampos@rdc.puc-rio.br

E. V. R. de Castro · H. C. de Jesus
Department of Chemistry, Espírito Santo Federal University,
Avenida Fernando Ferrari s/n, Campus de Goiabeira,
Vitória 29000-000 ES, Brazil

may have a strong influence on the method sensitivity, thereby causing calibration problems [17, 24]. GFAAS is a valuable alternative, since sensitivity variation due to the analyte form and matrix characteristics is much less pronounced if the stabilized temperature platform furnace (STPF) conditions are observed. However, in any case, a sample pre-treatment is always required for the determination of Ni in petroleum and their viscous products. Mineralization [9, 12, 18], extraction [2, 9], chromatographic separation [1, 2, 15], dilution [4, 16, 19], or emulsion formation [12–14, 21–23] have been proposed. Chromatography, mineralization, and extraction separations are time-consuming and increase the risks of contamination and losses, although calibration may be made simpler if an aqueous final solution is obtained. Dilution procedures are simple and proved to be efficient but the use of organic solvents is dangerous to health and the environment. Emulsion formation is also attractive, but the emulsion's short-term physical stability requires permanent analyst attendance. In the GFAAS determination of Ni in petroleum and its derivatives, expressive losses may be experienced in pyrolysis temperatures as low as 400 °C if no modifier is used; thus, the use of chemical modification is mandatory for this application [21–23]. Solid sampling (SS) avoids sample pre-treatment, as well as the risks of contamination and losses related to this step. SS-GFAAS was successfully applied to direct determination of trace elements in various matrices, such as coal [25, 26], polyamide [27], foods [28], vitamin complex and agricultural soil [29], ash, sludge, marine and river sediments [30], as well as biological tissue [31]. Limitations related to the sample homogeneity must be considered, due to the low sample mass. However, in the case of petroleum and other viscous samples this limitation is reduced. Thus, in the present work, a procedure for the direct determination of Ni in petroleum samples by SS-GFAAS is proposed.

## Experimental

### Instrumentation

The Ni GFAAS measurements were performed with a model Zeenit 60 (Analytik Jena, Germany) atomic absorption spectrometer, equipped with a transversally heated graphite atomizer and a Zeeman effect background corrector. Sampling was performed with a SSA6Z (Analytik Jena, Germany) solid sampling accessory. An Analytik Jena Ni hollow cathode lamp, operated at 5 mA was used as line source. The slit was fixed at 0.2 nm, and the 232.0 and 234.6-nm lines were used. The magnetic field was operated in the 2-field mode at 0.8, 0.4, and 0.2 T. A model AD-4 (Perkin Elmer, Norwalk, CT, USA) analytical micro-balance was used for sample weighing. All measurements were made in peak area mode. In the comparative procedure the Ni measurements were performed by FAAS using a model 1100B atomic absorption spectrometer (Perkin Elmer, Norwalk, CT, USA) with a continuum source (deuterium lamp) background corrector; an Analytik Jena Ni hollow cathode lamp, operated at 6 mA was used as line source ($\lambda$=232.0 nm); the slit was 0.2 nm and all measurements were made in the peak height mode within a 15-s observation window.

### *Materials, reagents, solutions, and samples*

Argon (99.99%, AGA, Rio de Janeiro, Brazil) was used as protective and carrier gas. Ultrapure water, obtained from a Master System apparatus (Gehaka, S. Paulo, Brazil) was used throughout. Analytical grade $HNO_3$ (Vetec, Rio de Janeiro, Brazil) was purified by sub-boiling distillation using an of Teflon sub-boiler apparatus (Hans Kuerner, Rosenheim, Germany). A 1,000 µg $mL^{-1}$ nickel stock solution was prepared by dilution of a Titrisol ampoule (Merck, Darmstadt, Germany) with 0.2% v/v $HNO_3$. Aqueous analytical solutions were prepared by dilution of the stock solution with 0.2% v/v $HNO_3$ solution. A 1,000 µg $g^{-1}$ organic nickel stock solution in oil (Conostan, Houston, USA) was also used. Organic analytical solutions were prepared by dilution of the stock solution with base-oil 75 (Spex, Metuchen, USA). The conventional 1,500 µg $mL^{-1}$ Pd modifier was prepared from a 10,000 µg $mL^{-1}$ palladium stock solution ($Pd(NO_3)_2$, Merck, Darmstadt, Germany). It contained 0.025% v/v Triton X 100 (Vetec, Rio de Janeiro, Brazil). The permanent modifier was prepared from a 5,000 µg $mL^{-1}$ $IrCl_3$ (Fluka, Buchs, Switzerland) stock solution in 10% v/v $HNO_3$. In the comparative procedure, xylene (Vetec, Rio de Janeiro, Brazil) was used as diluent. All plastic and glassware was washed with tap water, immersed in Extran (48 h), rinsed with tap and deionized water, and immersed in 20% v/v $HNO_3$ for at least 24 h. Before use, these materials were thoroughly rinsed with ultrapure water and oven-dried at 40° C, avoiding any contact with metallic surfaces and dust contamination. Contamination was always checked up by a strict blank control. The petroleum samples were obtained from Petrobras. NIST 1634c (Trace Elements in Fuel Oil) as well as ASTM CO 0403, 0311 and 0504 crude oils were used for validation.

### Procedures

#### *Proposed procedure*

The petroleum sample was manually shaken for homogenization and an aliquot (0.10–0.60 mg) was weighed onto the graphite cup of the solid sampling device using the micro-balance. Twenty microliters of the palladium modifier solution was then manually deposited over the sample. The graphite cup was inserted in the graphite furnace with the solid sampling accessory, and the Ni measurement was then performed. Calibration was carried out in a similar way, by weighing increasing masses (0.10 to 1.0 mg) of the same Ni aqueous standard (10 µg $mL^{-1}$ in 0.2% v/v $HNO_3$). The Zeeman AAS measurements were performed at 234.6 nm, at 0.40 T in the 2-field mode.

### *Comparative procedure (ASTM 5863-B[32])*

The petroleum sample was manually shaken for homogenization and an aliquot (1.0 g to the nearest 0.0001 g) was weighed in a 15-mL conical-ended screwed-cap plastic tube. The sample was diluted to 5.0 mL with xylene and homogenized. This solution was analyzed by FAAS using an air/acetylene flame. Analytical solutions were prepared by convenient dilution of the organic Ni stock solution with xylene, and the measurements were performed at 232.0 nm using $D_2$ background correction.

## Results and discussion

### Preliminary tests: matrix modifiers, spectral line, and magnetic field

The performance of conventional and permanent modifiers (Pd and Ir, respectively) were preliminarily investigated ($\lambda$= 232.0 nm and 2-field mode with 0.80 T). The furnace temperature program was similar to that used for the determination of Ni in vegetables oils [33]. A total of 600 µg of Ir was deposited onto the graphite cup using the coating procedure described by Grinberg et al. [34]. Low recoveries (<30% in the analysis of a petroleum sample of known concentration) indicated that this permanent modifier is not efficient and further investigation is necessary if it is to be used. In relation to the conventional modifier the tests were performed by dispensing 20 µL of a 1,000 µg $mL^{-1}$ Pd solution onto the graphite cup before or after the sample. If dispensed before the sample, the modifier solution was dried at 100 °C. Recoveries close to 100% were only observed by dispensing the modifier over the sample. However, erratic results still occurred, even using larger modifier solution volumes. This behavior was attributed to an eventual poor contact between the modifier and the sample. Thus, Triton X 100 was added to the Pd modifier solution, at a final concentration of 0.025% v/v, and the modifier solution volume dispensed kept at 20 µL. In this way, good repetitiveness was attained. Due to the high Ni concentration normally present in petroleum and in order to keep the objective of the procedure, that is, the avoidance of any sample pre-treatment, instrumental ways of lowering the sensitivity were investigated. This was attained by using the 234.6-nm secondary line and the 2-field mode with an intensity of 0.40 T. In this magnetic field a 30% sensitivity drop was observed. For the 0.20-T field the sensitivity drop was even larger (75%). However, accurate background correction was not possible in such a low field.

### Optimization of the proposed procedure

The multivariate optimized factors were the pyrolysis ramp and temperature, atomization temperature, and the Pd modifier mass. A petroleum sample was used. Initially, a complete factorial design ($2^4$) was followed, and the factor pyrolysis ramp has not shown statistic significance ($p>$ 0.05), in contrast to the other factors. However, the F test showed lack of fit as well as low $R^2$ values indicating that the proposed linear model was not adequate. Thus, the previous significantly important factors were optimized by a central composite design. The different levels are shown in Table 1. The Pareto diagrams (Fig. 1) show the significant effects ($p<0.05$). The $R^2$ adjusted value was 0.7264. The critical points were 1,097 °C for the pyrolysis temperature, 2,552 °C for the atomization temperature, and 29 µg for the Pd mass. The drying ramp and temperature were further univariate optimized. A slow drying ramp was necessary as well as a high drying temperature in order to avoid sample projection in the pyrolysis step. The optimized furnace temperature program is shown in Table 2. The petroleum sample masses ranged from 0.10 to 0.60 mg.

### Calibration

Inorganic Ni aqueous analytical curves were compared with organic Ni analytical curves. Both curves showed good linearity and no significant difference (Student t-test, $p<$ 0.05) between their slopes was observed. Thus, aqueous analytical calibration could be chosen.

### Analytical figures of merit

The limit of detection at the elected conditions ($\lambda$= 234.6 nm, 0.4 T, and temperature program as in Table 2) calculated according the IUPAC (3 s; $n$=10) was 0.23 ng.

**Table 1** Studied factor and their respective levels for the central composite design

| | Level | | | | |
|---|---|---|---|---|---|
| Factor | −1.68 | −1 | 0 | +1 | +1.68 |
| Pyrolysis temperature (°C) | 848 | 950 | 1,100 | 1,250 | 1,352 |
| Atomization temperature (°C) | 2,416 | 2,450 | 2,500 | 2,550 | 2,584 |
| Pd mass (µg) | 3 | 10 | 20 | 40 | 47 |

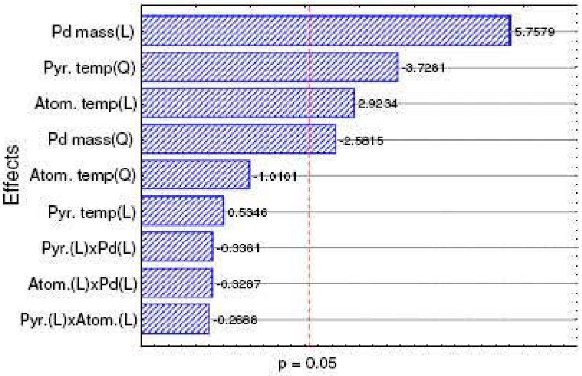


**Fig. 1** Pareto chart of standardized effects for the central composite design. *L* and *Q* mean linear and quadratic behavior, respectively

The characteristic mass was 45 pg. Linearity was observed at least up to 11 ng of Ni. Coefficients of variation of 8 and 7% were observed in the analysis of the NIST 1634c ($n$=5) and ASTM CO0504 ($n$=10) reference materials, respectively. The total determination cycle lasted 5 min, equivalent to a sample throughput of 6 $h^{-1}$ for duplicate determinations.

### Validation

The validation of the proposed procedure was performed by the determination of Ni in certified reference materials and by comparison with a validated independent method (ASTM 5863-B [32]). The results are displayed in Table 3. No statistically significant difference was observed between the reference values and those obtained by the proposed method, in the analysis of the reference materials (Student t-test, $p<0.05$). Also, good agreement was found between the results arising from the proposed and comparative procedures in the analysis of the petroleum samples.

**Table 2** Optimized furnace temperature program for the determination of Ni in petroleum samples by SS-GFAAS using Pd[a] as modifier

| Step | Operation | Temperature (°C) | Rate (°C $s^{-1}$) | Hold (s) | Gas flow |
|---|---|---|---|---|---|
| 1 | Drying | 90 | 10 | 5 | Max. |
| 2 | Drying | 150 | 10 | 5 | Max. |
| 3 | Drying | 350 | 2 | 10 | Max. |
| 4 | Pyrolysis | 1,100 | 10 | 30 | Max. |
| 5 | AZ[b] | 1,100 | 0 | 6 | Stop |
| 6 | Atomize | 2,550 | 2,200 | 5 | Stop |
| 7 | Cleanout | 2,650 | 1,000 | 5 | Max. |

[a] 20 µL of 1,500 µg $mL^{-1}$ Pd in 0.025% Triton X 100
[b] Auto-zero

**Table 3** Determination of Ni ($n$=3) by the proposed and comparative procedures in certified reference materials and petroleum samples (A to N)

| Sample | Ni (µg $g^{-1}$) Reference value[a] | Proposed procedure[a] | Comparative procedure[a] |
|---|---|---|---|
| NIST 1634c | 17.5±0.2 | 17.7±1.5[b] | nd[d] |
| ASTM CO 0403 | 10.4±1.3 | 12.4±1.6 | 13.3±0.4 |
| ASTM CO 0311 | 10.2±2.6 | 11.4±1.8 | 11.9±0.4 |
| ASTM CO 0504 | 52.4±7.1 | 57.0±4.0[c] | 54.2±0.3 |
| A | – | 11.2±0.1 | 12.5±0.6 |
| B | – | 19.7±1.5 | 19.4±0.6 |
| C | – | 15.5±1.5 | 14.3±0.6 |
| D | – | 23.2±2.4 | 21.3±1.1 |
| E | – | 14.7±0.5 | 14.3±0.6 |
| F | – | 11.9±1.9 | 11.2±0.6 |
| G | – | 11.6±0.2 | 11.4±0.6 |
| H | – | 19.2±2.4 | 22.1±1.4 |
| I | – | 8.4±0.7 | 7.9±0.6 |
| J | – | 20.8±3.3 | 19.6±0.6 |
| K | – | 24.8±0.3 | 22.5±0.6 |
| L | – | 9.4±0.4 | 8.9±0.6 |
| M | – | 11.7±0.6 | 10.4±0.6 |
| N | – | 34.7±2.4 | 35.5±1.6 |

[a] ±standard deviation
[b] $n$=5
[c] $n$=10
[d] Not determined

## Conclusions

The conventional Pd modifier dispensed over the sample proved to be more efficient than pre-treating the graphite cup surface with Pd or Ir. This apparent contrast with previous work [21–23] may be due to the fact that these authors diluted or emulsified the samples before analysis, whereas no sample pre-treatment was performed in the present work. The addition of Triton X 100 to the modifier solution was indispensable for good repetitiveness. Calibration with aqueous analytical solutions was feasible after multivariate optimization. In this way, no statistical difference was observed between the proposed and comparative procedures in the analysis of petroleum samples. Similar concordance was observed in relation to the certified and reference materials investigated. The dynamic range was 0.52 to 110 µg $g^{-1}$, considering sample masses from 0.10 to 0.60 mg. This range was attained by using a secondary line and alternative field intensity. All investigated samples were within this range. Good repetitiveness was observed even with such small sample masses, proving sufficient sample homogeneity after just a manual shake. No sample pre-treatment was required, not even dilution, avoiding the use organic solvents that are harmful to human health and the environment. The proposed method has the potential to be extended to other analytes and highly viscous samples.

## References

1. Fish RH, Komlenic JJ, Wines BK (1984) Anal Chem 56:2452–2460
2. Márquez N, Ysambertt F, De La Cruz C (1999) Anal Chim Acta 395:343–349
3. Reynolds JG (2001) Pet Sci Technol 19:979–1007
4. Fabec JL, Ruschak ML (1985) Anal Chem 57:1853–1863
5. Bettinelli M, Tittarelli P (1994) J Anal At Spectrom 9:805–812
6. Kubo H, Bernthal R (1978) Anal Chem 50:899–903
7. Iwasaki K, Tanaka K (1982) Anal Chim Acta 136:293–299
8. Denoyer ER, Siegel LA (1987) Anal Chim Acta 192:361–366
9. Khuhawar MY, Lanjwani SN (1996) Talanta 43:767–770
10. Brown RJ (1985) Spectrochim Acta Part B 38:283–289
11. Hausler DW, Carlson R (1991) Spectrochim Acta Rev 14:125–140
12. Souza RM, Silveira CLP, Aucélio RQ (2004) Anal Sci 20:351–355
13. Lord CJ (1991) Anal Chem 63:1594–1599
14. Al-Swaidan HM (1996) Talanta 43:1313–1319
15. Duyck C, Miekeley N, Porto da Silveira CL, Szatmari P (2002) Spectrochim Acta Part B 57:1979–1990
16. Kahen K, Strubinger A, Chirinos JR, Montaser A (2003) Spectrochim Acta Part B 58:397–413
17. Lang I, Šebor GS, Sychra V, Kolihová D, Weisser O (1976) Anal Chim Acta 84:299–305
18. Platteau O, Carrillo M (1995) Fuel 74:761–767
19. Hammond JL, Lee YI, Noble CO, Beck JB, Proffitt CE, Sneddon J (1998) Talanta 47:261–266
20. Bruhn C (1983) Anal Chim Acta 147:193–198
21. Meeravali NN, Kumar SJ (2001) J Anal Atom Spectrom 16:527–532
22. Vale MGR, Damin ICF, Klassen A, Silva MM, Welz B, Silva AF, Lepri FG, Borges DLG, Heitmann U (2004) Microchem J 77:131–140
23. Damin ICF, Vale MGR, Silva MM, Welz B, Lepri FG, Santos WNL, Ferreira SLC (2005) J Anal Atom Spectrom 20:1332–1336
24. Šebor G, Lang I, Kolihova D, Weisser O (1982) Analyst 107:1350–1355
25. Vale MGR, Silva MM, Welz B, Lima EC (2001) Spectrochim Acta Part B 56:1859–1873
26. Silva AF, Borges DLG, Welz B, Vale MGR, Silva MM, Klassen A, Heitmann U (2004) Spectrochim Acta Part B 59:841–850
27. Resano M, Aramendia M, Volynsky AB, Belarra MA (2004) Spectrochim Acta Part B 59:523–531
28. Coskun N, Akman S (2005) Spectrochim Acta Part B 60:415–419
29. Belarra MA, Crespo C, Martinez-Garbayo MP, Resano M (2003) Spectrochim Acta Part B 58:1847–1858
30. Silva AF, Welz B, Curtius AJ (2002) Spectrochim Acta Part B 57:2031–2045
31. Hornung M, Krivan V (1997) J Anal At Spectrom 12:1123–1130
32. Standard test methods for determination of nickel, vanadium, iron, and sodium in crude oils and residual fuels by flame atomic absorption spectrometry (method 5863-B). ASTM International, reapproved 2005
33. Reyes MM, Campos RC (2006) Talanta (in press)
34. Grinberg P, Campos RC (2001) Spectrochim Acta Part B 56:1831–1843

Anal Bioanal Chem (2006) 385: 1562–1569
DOI 10.1007/s00216-006-0585-0

ORIGINAL PAPER

**Geisamanda Pedrini Brandão ·**
**Reinaldo Calixto de Campos · Aderval Severino Luna ·**
**Eustáquio Vinicius Ribeiro de Castro ·**
**Honério Coutinho de Jesus**

# Determination of arsenic in diesel, gasoline and naphtha by graphite furnace atomic absorption spectrometry using microemulsion medium for sample stabilization

Received: 15 March 2006 / Revised: 23 May 2006 / Accepted: 1 June 2006 / Published online: 25 July 2006

**Abstract** A procedure for the determination of As in diesel, gasoline and naphtha at µg $L^{-1}$ levels by GFAAS is proposed. Sample stabilization was achieved by the formation of three component solutions prepared by mixing appropriate volumes of the samples propan-1-ol and nitric acid aqueous solution. This mixture resulted in a one-phase medium, which was indefinitely stable. No changes in the analyte signals were observed over several days in spiked samples, proving long-term stabilization ability. The use of conventional (Pd) and permanent (Ir) modification was investigated and the former was preferred. Central composite design multivariate optimization defined the optimum microemulsion composition as well as the temperature program. In this way, calibration using aqueous analytical solutions was possible, since the same sensitivity was observed in the investigated microemulsion media and in 0.2% v/v $HNO_3$. Coefficients of correlation larger than 0.999 and an As characteristic mass of 22 pg were observed. Recoveries ($n$=4) obtained from spiked samples were 98±4, 99±3 and 103±5%, and the limits of detection in the original samples were 1.8, 1.2 and 1.5 µg $L^{-1}$ for diesel, gasoline and naphtha, respectively. Validation was performed by the analysis of a set of commercial samples by independent comparative procedures. No significant difference (Student's $t$-test, $p$<0.05) was observed between comparative and proposed procedure results. The total determination cycle lasted 4 min for diesel and 3 min for gasoline and naphtha, equivalent to a sample throughput of 7 $h^{-1}$ for diesel and 10 $h^{-1}$ for gasoline and naphtha.

**Keywords** Arsenic · Petroleum derivates · Stabilization as microemulsion · Graphite furnace atomic absorption spectrometry (GFAAS)

G. P. Brandão · R. C. de Campos (✉)
Department of Chemistry, Pontifical Catholic University,
Rua Marques de S. Vicente, 225, Gávea,
22453-900 Rio de Janeiro, RJ, Brazil
e-mail: rccampos@rdc.puc-rio.br
Fax: +55-21-31141309

A. S. Luna
Department of Analytical Chemistry,
Rio de Janeiro State University,
Rua S. Francisco Xavier, s/n, Maracanã,
20550-900 Rio de Janeiro, RJ, Brazil

E. V. R. de Castro · H. C. de Jesus
Department of Chemistry, Espírito Santo Federal University,
Avenida Fernando Ferrari, s.n, Campus de Goiabeiras,
29000-000 Vitória, ES, Brazil

## Introduction

The determination of trace elements in petroleum derivates is of key importance. Their presence in products such as gasoline, diesel and naphtha is related to poor performance and reduced stability of these products. Certain metallic and metalloid species in these derivates can catalyze oxidative reactions, decreasing their thermal stability to an undesirable extent [1]. In addition, their content of potentially toxic elements must be evaluated since these elements are released to the atmosphere due to the use of petroleum derivate fuels as energy source in oil-fired power plants and automobiles [2]. Concerning As, even traces of this element can cause severe and irreversible catalyst poisoning [3]. Thus, its accurate quantification in naphtha samples is important for the refining process and petrochemical industries. It is also of environmental importance, due to the toxicological properties of its compounds.

Trace elements in petroleum derivates have been determined by various analytical techniques. The instrumental advance of inductively coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma-optical emission spectrometry (ICP-OES) permitted the direct handling of hydrocarbon blends [4–7]. Problems such as the formation of carbonaceous residues and the different behavior of organic in relation to aqueous solutions were reduced by the addition of oxygen in the carrier gas [4, 5] or the use of water-in-oil emulsions [6–8]. However ICP-MS, although a multielementar and highly sensitive technique, is still relatively expensive, while ICP-OES does not show the necessary sensitivity in many situations. Hydride generation followed by a convenient atomic spectrometric technique can also be used for hydride forming elements [9, 10], but in general only after sample mineralization.

An advantageous alternative for the determination of trace elements in petroleum fractions and distillates is the graphite furnace atomic absorption spectrometry (GFAAS). Although still not multielementar, its sensitivity is adequate for most cases and a minimum sample pretreatment is necessary [1, 11, 12]. GFAAS has also been proposed for determination of As in such samples. Accurate determination depends on many factors such as the analyte form, type of matrix and solvent, as well as the sample preparation procedure. Arsenic high volatility must also be considered. Diverse sample pretreatments such as extraction to aqueous phase [9, 13], combustion in an oxygen bomb [10] and chemical mineralization [9, 13, 14], lead to a final aqueous medium. This is advantageous for calibration, but problems related to contamination and losses may occur. Moreover, these procedures are, in general, time consuming. An easier procedure, is the direct analysis in organic medium by direct sample introduction [15, 16] or by the formation of emulsions [17, 18]. However, if no previous sample mineralization is performed, sufficiently high pyrolysis temperatures must be used to guarantee efficient matrix removal. Expressive losses of As in organic matrices are observed in temperatures as low as 200–400 °C if no modifier is used and, therefore, the use of chemical modification is mandatory for this application [15–17, 19–21]. Comparative studies have recommended the use of palladium nitrate as a modifier for As, either alone or mixed with magnesium nitrate. In this way, pyrolysis temperatures from 1,000 to 1,400 °C are reported [16, 17, 20]. Other modifiers such as nickel nitrate [21], lantanium [15], ruthenium [17, 20] and iridium [18], have also been recommended. Both conventional—Pd/$MgNO_3$, $Pd(NO_3)_2$, $Ni(NO_3)_2$ and $La_2O_3$—as well as permanent modification (Ru and Ir) were proposed. Sample stability must also be considered, since metals dissolved in organic liquids at the µg $L^{-1}$ level are readily lost [1, 18]. Thus, analyte stabilization is mandatory for guaranteeing sample representativeness as well as repetitiveness throughout the analysis, although few studies in the related literature have considered this point. Previous works [1, 22–24] have shown that different trace elements were successfully stabilized in these samples by the formation of three component solutions (microemulsions). Microemulsions are spontaneously and immediately formed after mixing their components, resulting in a one-phase, homogeneous, transparent and indefinitely stable medium, in contrast to emulsions [17, 18]. Such stability dispenses any further shaking during analysis [17, 18], permitting the full exploitation of the autosampler capabilities. Moreover, dilution factors are small, avoiding prohibitive impoverishment of the overall limit of detection.

Thus, the present work investigates the determination of As in gasoline, diesel and naphtha samples by GFAAS, also taking the samples stability into account. Procedures for the determination of this element in these samples after the formation of microemulsions are proposed.

## Experimental

### Instrumentation

The As GFAAS measurements were performed with a model Zeenit 60 (Analytik Jena, Germany) atomic absorption spectrometer, equipped with a transversally heated graphite atomizer, Zeeman background correction as well as an AS-52 autosampler. An Analytik Jena As hollow cathode lamp operated at a current of 9 mA was used as line source. The measurements were performed at 193.7 nm, with the slit fixed at 0.5 nm. Additionally, the 2-field mode at 0.8 Tesla was used. All measurements were made in peak area, with a 4s integration time. For the naphtha comparative procedure, the As measurements were performed with a model AA12/1475 Varian atomic absorption spectrometer coupled to a VGA-76 vapor generation accessory (both Varian Techtron, Melbourne, Australia); an Analytik Jena As hollow cathode lamp, operated at 11 mA and 193.7 nm was used as line source; a windowless quartz T cell (5 mm internal diameter, 13 cm long) heated at approximately 900 °C by an air-acetylene flame was used as absorption cell; the slit was 0.5 nm and all measurements were made in peak height with a 15 s observation time window.

### *Materials, reagents, solutions and samples*

Argon 99.99 (AGA, Rio de Janeiro, Brazil) was used as a protective and carrier gas. Ultra pure water, obtained from a Gehaka Master System apparatus (Gehaka, S. Paulo, Brazil) was used throughout. Analytical grade $HNO_3$ (Vetec, Rio de Janeiro, Brazil) was purified by subboiling distillation using a Teflon$^R$ subboiler apparatus (Hans Kuerner, Rosenheim, Germany). A 1,000 mg $L^{-1}$ As stock solution was prepared by adequate dilution of a Titrisol ampoule (Merck, Darmstadt, Germany) with 0.2% v/v $HNO_3$. Aqueous analytical solutions were prepared by further convenient dilutions of this solution also with 0.2% v/v $HNO_3$. Organic analytical solutions were prepared by adequate dilution of a 100 mg $Kg^{-1}$ As stock solution in oil (Spex, Metuchen, NJ, USA) with *n*-hexane (Vetec, Rio de Janeiro, Brazil). Propan-1-ol (Vetec, Rio de Janeiro, Brazil) was used for preparing the microemulsions while $Pd(NO_3)_2$ (10,000 mg $L^{-1}$, Merck, Darmstadt, Germany), $IrCl_3$ (5,000 mg $L^{-1}$ in 10% $HNO_3$ v/v, Fluka, Buchs, Switzerland), and $Ni(NO_3)_2$ (1% w/v, Merck, Darmstadt, Germany) were used for preparing the modifiers. Ammonium hydroxide (Vetec, Rio de Janeiro, Brazil), HCl (Vetec, Rio de Janeiro, Brazil), $H_2SO_4$ (Merck, Rio de Janeiro, Brazil), $(NH_4)_3PO_4$ (Vetec, Rio de Janeiro, Brazil) and $KMnO_4$ (Vetec, Rio de Janeiro, Brazil), all analytical reagent grade were used for the comparative procedures. The following solutions were also used (all prepared with analytical reagent grade): 5% w/v NaOCl (Vetec, Rio de Janeiro, Brazil); 70% v/v $H_2SO_4$ (Merck, Rio de Janeiro, Brazil); 30% v/v $H_2O_2$ (Vetec, Rio de Janeiro, Brazil); saturated $(NH_4)_2C_2O_4$ (Vetec, Rio de Janeiro, Brazil); 10% m/v KI (Vetec, Rio de Janeiro, Brazil); 0.6% m/v $NaBH_4$ (Vetec, Rio de Janeiro, Brazil) in 0.5% m/v NaOH (Vetec, Rio de Janeiro, Brazil); 80% v/v HCl (Vetec, Rio de Janeiro, Brazil); 5% m/v $I_2$ (Isofar, Rio de Janeiro, Brazil) in toluene (Vetec, Rio de Janeiro, Brazil). In the naphtha analysis by the comparative procedure, $N_2$ (AGA, Rio de Janeiro, Brazil) was used as carrier gas.

All plastic and glassware was washed with tap water, immersed in Extran (48 h), rinsed with tap and deionized water, and immersed in 20% v/v $HNO_3$ for, at least, 24 h. Before use, these materials were thoroughly rinsed with ultrapure water and oven dried at 40 °C, avoiding any contact with metallic surfaces and dust contamination. Contamination was always checked by a strict blank control. Commercial gasoline and diesel samples were collected in polyethylene bottles in the gas stations of the cities of Rio de Janeiro and Vitória (Brazil), and brought immediately to the laboratory for the experiments. Naphtha samples were supplied by local industries.

### Procedures

#### *Proposed procedure*

The samples (diesel, gasoline and naphtha) were immediately stabilized after collection. The stabilization was achieved by mixing the sample with propan-1-ol and a 50% v/v $HNO_3$ solution at 3.6:6.3:0.1, 6.0:3.9:0.1 and 5.5:4.4:0.1 volume ratios for diesel, gasoline and naphtha, respectively. A total of 15 µl of the stabilized sample as well as 5 µl of the $Pd(NO_3)_2$ modifier solution were then injected in the graphite atomizer. Calibration was performed with aqueous (0.2% v/v $HNO_3$) analytical solutions.

#### *Comparative procedures*

*UOP Method 946-96, As determination in naphtha* In short, the naphtha samples (100 g to the nearest 0.01 g) were sequentially extracted with 5% w/v NaOCl, 70% v/v $H_2SO_4$, and water. All aqueous layers were transferred to the same Kjeldahl flask, followed by the addition of concentrated $HNO_3$, $H_2SO_4$, and $H_2O_2$. After heating, saturated $(NH_4)_2C_2O_4$ solution was added, the mixture was heated again, cooled, and transferred to a volumetric flask. After pre-reduction with 10% w/v KI and using 0.6% m/v $NaBH_4$ in 0.5% m/v NaOH as reductant, arsenic was determined in this solution by HG-AAS in HCl medium [9].

*EPA Method 3031, As determination in diesel* In short, the $KMnO_4$ solution was added to a 2 g (±0.01) sample. The mixture was warmed while stirring, followed by the sequential addition of concentrated $H_2SO_4$, $HNO_3$, and HCl as well as water. The digestate was then filtered and the filtrate collected in a beaker. After washing the digestion beaker and filter paper with hot HCl, the volume was reduced by heating, followed by the addition of concentrated $NH_4OH$, $(NH_4)_3PO_4$ and water. This mixture was then filtered, and the filtrate collected in another beaker. This new filtrate was heated and the volume was reduced almost to dryness. The residual solution was then cooled and sufficient volume of concentrated $HNO_3$ was added. This solution was then transferred to a volumetric flask. Arsenic determination was performed in this solution by GFAAS using $Pd(NO_3)_2$ as modifier [14].

*As determination in gasoline* A 5% m/v $I_2$ in toluene solution was added to a 20.0-ml gasoline sample contained in a funnel. The funnel was shaken and left for 60 s. The extraction was then performed with 1% v/v $HNO_3$. The aqueous phase was collected in a beaker, and two further identical extractions were carried out. The pooled aqueous extract was evaporated almost to dryness, cooled, and transferred to a volumetric flask. One volume of the solution was made and analyzed by GFAAS, using $Ni(NO_3)_2$ as modifier [13].

## Results and discussion

### As stabilization in the samples

Preliminarily, the stability of As in diesel, gasoline, and naphtha samples was investigated using spiked samples. For inorganic As, the samples were spiked using 10 µg $ml^{-1}$ working solutions prepared by dilution of the 1,000 µg $ml^{-1}$ standard inorganic solution with propan-1-ol. For organic As, the dilution of the 100 µg $g^{-1}$ standard in oil was performed in *n*-hexane. The spiked samples were transferred to autosampler cups of different materials and periodically measured using the temperature program shown in Table 1. This is not the final optimized program, but since in this part of the experiment relative signals are enough for the investigation, this was not a problem. In order to avoid evaporation, the autosampler cups were closed tightly between each measurement. Any residual evaporation was compensated for by weighing the samples before each measurement. Palladium (10 µg) was used as a modifier. A significant signal drop was observed over time for both As species in these samples (Fig. 1). In general, the drop is larger for inorganic (Fig. 1a) than for organic (Fig. 1b) As and in gasoline and naphtha in comparison to diesel

**Table 1** Temperature program for As measurements in diesel, gasoline, and naphtha samples in the stability studies

| Steps | Temp (°C) | Rate (°C/s) | Hold (s) |
|---|---|---|---|
| Drying | 100 | 5 | 10 |
| Drying | 200 | 2 | 5 |
| Pyrolysis | 1,200 | 50 | 20 |
| AZ | 1,200 | 0 | 5 |
| Atomize | 2,500 | FP | 3 |
| Cleanout | 2,650 | 1,000 | 2 |

*AZ* Auto-zero; *FP* full power

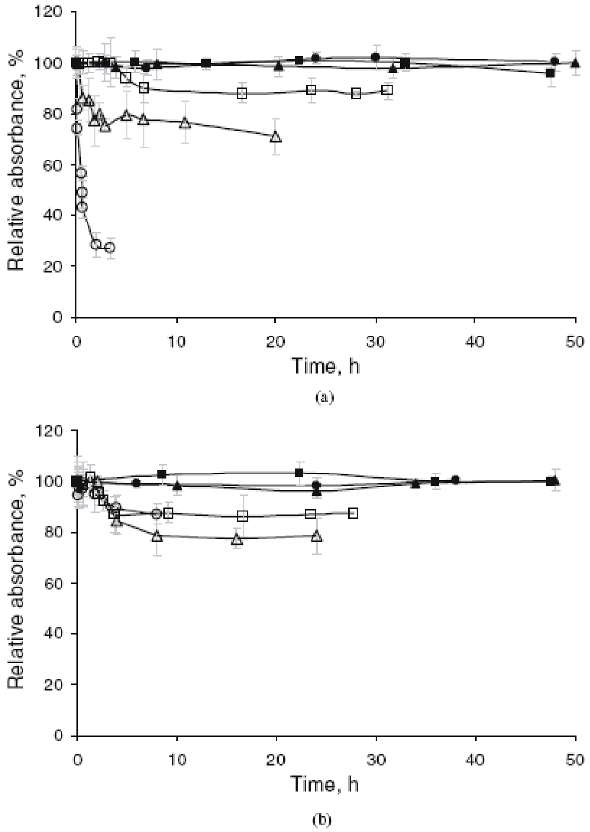


**Fig. 1** Stability of As **a** spiked with inorganic and **b** organic As in: diesel-microemulsion (*filled squares*); gasoline-microemulsion (*filled triangles*); naphtha-microemulsion (*filled circles*); diesel (*empty squares*); gasoline (*empty triangles*) and naphtha samples (*empty circles*) stored in polyethylene cups

samples. Fig. 1 shows the results relatively to polyethylene cups, although these drops were even stronger if the samples were stored in Teflon$^R$ or glass containers (not shown). The same experiment was performed but using a comparative method [13], and similar results were found, excluding any artifact possibility related to the direct GFAAS determination. Similar losses were also observed in non spiked gasoline samples, although similar experiments with non spiked naphtha and diesel could not be performed due to the low As level of the samples available. Thus, further experiments must be performed to make this point clear. Sample stabilization was achieved by the formation of three component solutions, prepared by mixing appropriate volumes of the sample, propan-1-ol and $HNO_3$ aqueous solution, forming a microemulsion. No change in the As signal was observed over several days for samples contained in polyethylene cups, proving long-term stabilization. Similar results were found using cups of Teflon$^R$ and glass. The volume proportion of the microemulsion components are those described in section Proposed procedure. For scale reasons, Fig. 1 shows the results relatively to the first two days only, although the experiments lasted for one week or more.

## Multivariate optimization of the proposed method

The optimization of the microemulsion composition (proportion) as well as the furnace temperature program for each kind of sample was performed by multivariate optimization. Palladium nitrate was used as the modifier, and its deposited mass (10 µg) was kept constant throughout the optimization experiment. The variables related to the microemulsion composition were the nitric acid final concentration and the sample/propan-1-ol volume ratio. The $HNO_3$ solution volume and microemulsion total volume were kept constant at 100 µl and 10 ml, respectively. The pyrolysis and atomization temperatures as well as the pyrolysis ramp were the variables related to the furnace temperature program. In principle, a complete factorial design ($2^5$) was performed, with five factors and two levels. The $2^5$ (32) experiments were made at a random order. The data were analyzed by using the Statistica 6.0 Statsoft software and the $2^{(k-p)}$ standard design [25]. Table 2 shows the studied variables and their respective levels. For all samples, the variable A (pyrolysis ramp) did not shown statistic significance ($p>0.05$), in contrast to variables B (pyrolysis temperature), C (atomization temperature), D ($HNO_3$ concentration), and E (sample/ propan-1-ol volume ratio). The $R^2$ values were less than 0.50 for all samples. Since the F-test showed lack of fit and lower $R^2$, the proposed linear model was not adequate. Thus, a central composite design was used. The variable A, not significant in the linear model, was kept constant at 100 °C/s. For the others variables, 16 ($2^4$) experiments related to the factorial design, 8 (2×4) star experiments ($\alpha=\pm16^{1/4}$) and 5 central experiments were performed. The different levels are shown in Table 3. The 29 experiments were randomly performed. The 29 data ($n$=3) were analyzed using the Statistica 6.0 software (central composite, non-factorial, surface designs). The Pareto diagrams (Fig. 2) show the significant effects ($p<0.05$). For the diesel sample, the significant effects (Fig. 2a) were B and E (linear behavior) and C and E

**Table 2** Studied variables and their respective symbols and levels for the $2^5$ factorial design

| Variable symbols | Description | Levels | | | | | |
|---|---|---|---|---|---|---|---|
| | | Diesel | | Gasoline | | Naphtha | |
| | | −1 | +1 | −1 | +1 | −1 | +1 |
| A | Pyrolysis ramp (°C/s) | 50 | 100 | 50 | 100 | 50 | 100 |
| B | Pyrolysis temperature (°C) | 900 | 1,300 | 900 | 1,300 | 900 | 1,300 |
| C | Atomization temperature (°C) | 2,400 | 2,600 | 2,400 | 2,600 | 2,400 | 2,600 |
| D | $HNO_3$ concentration (% v/v) in the microemulsion | 0.4 | 0.8 | 0.4 | 0.8 | 0.4 | 0.8 |
| E | Sample/propan-1-ol volume ratio | 0.40 | 0.67 | 0.50 | 1.45 | 0.50 | 1.72 |

**Table 3** Studied variables and their respective levels for the central composite design. Variable symbols as in Table 2

| Variables | Levels | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Diesel | | | | | Gasoline | | | | | Naphtha | | | | |
| | −2 | −1 | 0 | +1 | +2 | −2 | −1 | 0 | +1 | +2 | −2 | −1 | 0 | +1 | +2 |
| B | 800 | 900 | 1,000 | 1,100 | 1,200 | 500 | 700 | 900 | 1,100 | 1,300 | 725 | 850 | 975 | 1,100 | 1,225 |
| C | 2,450 | 2,500 | 2,550 | 2600 | 2,650 | 2,450 | 2,500 | 2,550 | 2,600 | 2,650 | 2,350 | 2,425 | 2,500 | 2,575 | 2,650 |
| D | 0.15 | 0.30 | 0.45 | 0.60 | 0.75 | 0.15 | 0.30 | 0.45 | 0.60 | 0.75 | 0.15 | 0.30 | 0.45 | 0.60 | 0.75 |
| E | 0.31 | 0.40 | 0.49 | 0.58 | 0.67 | 0.70 | 1.04 | 1.38 | 1.72 | 2.06 | 0.70 | 1.04 | 1.38 | 1.72 | 2.06 |

(quadratic behavior), as well as the interactions of B and D as well as B and E. The $R^2$ value was 0.731. For the gasoline sample, the significant effects (Fig. 2b) were D and E (linear behavior) and B, C, D and E (quadratic behavior). The $R^2$ value was 0.720. For naphtha the significant effects (Fig. 2c) were B, C, D and E (linear behavior) and B (quadratic behavior), as well as the interactions of B and C; C and D; and B and E. The $R^2$ value was 0.747. Other statistical techniques such as the analysis of normal probability plots and the desirability functions have shown similar results. The optimized final $HNO_3$ concentrations in the microemulsions were 0.47, 0.39 and 0.49% (v/v) and the sample/propan-1-ol volume ratio were 0.57, 1.51 and 1.25 for diesel, gasoline and naphtha, respectively. The optima atomization and pyrolysis temperatures are shown in Table 4. Note that these values must not be taken so exactly as they may be due to the unusual values found. Since the fitted surfaces (not shown) along the temperature axis just show a smooth curvature in the proximity of the maximum values, a ±50 °C variation can be accepted without any significant change in the sensitivity.

The drying ramp and drying temperature were further univariately optimized. For the diesel samples, a slower drying ramp was necessary as well as a higher drying temperature in order to avoid sample projection in the pyrolysis step. The final optimized furnace programs for the GFAAS determination of As in diesel, gasoline and naphtha stabilized as microemulsions are shown in Table 4.

## Conventional and permanent modifiers

The performance of conventional and permanent modifiers (Pd and Ir, respectively) was investigated. In relation to the conventional modifier, 15 µl of the stabilized sample was dispensed into the furnace, followed by the addition of 5 µl of 2,000 mg $L^{-1}$ Pd solution. In the investigation of the permanent modifier, Ir was deposited onto the platform using the coating procedure described by Grinberg et al. [26]. A total of 600 µg of Ir was deposited, by pipetting 20 µl of the 5,000 mg $L^{-1}$ Ir solution and subjecting the tube to the temperature program given by Grinberg et al. [26], repeating this procedure six times. The modifier efficiency was investigated by pyrolysis temperature curves made with spiked samples. Inorganic as well as organic As were spiked and the samples stabilized as microemulsion, as already described. As losses in temperatures as low as 300–400 °C occurred using Ir as permanent modifier. However, stabilization was achieved from 400 °C on (Fig. 3). This behavior may be attributed to the partial formation of an As volatile species that is not thermally stabilized by the permanent modifier. This proposal is supported by the fact that these thermal losses were even larger for spiked samples stored for a longer

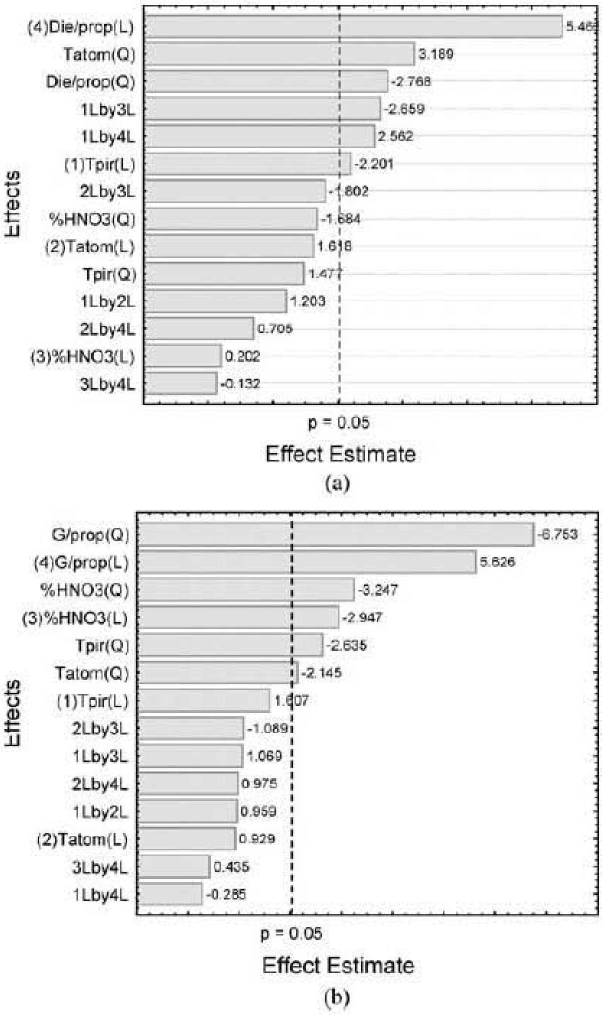
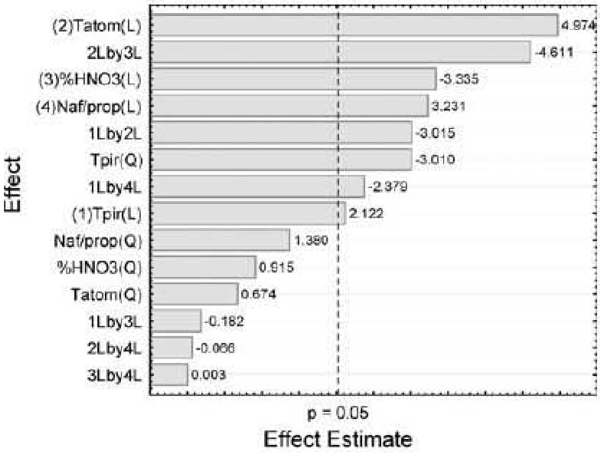


**Fig. 2** Pareto charts of standardized effects for the central composite design for **a** diesel, **b** gasoline, and **c** naphtha samples stabilized as microemulsions. (*L*) and (*Q*) mean linear and quadratic behavior, respectively

**Figure 2** (continued)



(c)

time, as Fig. 3 also shows. The same tests were made by depositing 900 and 1,200 µg of Ir onto the platform. Similar losses were observed as well as no sensitivity improvement. The conventional modifier (Fig. 4) led to lower absorbance values at temperatures of 300 °C. However, the absorbance signal recovered for higher temperatures and turned constant from 600 °C on. In face of these results, conventional modification using Pd was preferred as the modification strategy in the present work. It is worth to observe that along the whole experiment background attenuation was always within the range of the background corrector. The masses of Pd were then optimized (univariate), using the optimized furnace temperature program and microemulsion composition. They were 10, 12.5, and 12.5 µg for diesel, gasoline and naphtha samples, respectively.

### Calibration

Aqueous analytical curve (0.2% $HNO_3$ v/v; $y=0.0028\times$ ($\pm0.0001$), $R^2=0.9994$) was compared with analytical curves derived from spiking low As level samples stabilized as microemulsion with inorganic As dissolved in propan-1-ol. Individual analyte addition on different microemulsion stabilized samples, was also investigated. Microemulsions using identical volume ratio of n-hexane instead of the samples were investigated. No significant difference (Student's $t$-test, $p<0.05$) was observed for the curves' slopes: Diesel, $y=0.0029\times$ ($\pm0.0001$), $R^2=0.9916$; gasoline, $y=0.0030\times(\pm0.0001)$, $R^2=0.9995$; naphtha, $y=0.0031\times(\pm0.0001)$, $R^2=0.9990$; $n$-hexane, $y=0.0030\times$ ($\pm0.0001$), $R^2=0.9993$. That is, the same sensitivity was observed in all cases, permitting calibration using aqueous analytical solution.

### Analytical figures of merit

The limits of detection (LOD) at the optimized conditions were 1.8, 1.2 and 1.5 µg $L^{-1}$ in the original diesel, gasoline and naphtha samples, respectively. The As characteristic mass was 22 pg. Linearity was observed at least up to 100 µg $L^{-1}$. The total determination cycle lasted 4 min for diesel and 3 min for gasoline and naphtha, equivalent to a sample throughput of 7 $h^{-1}$ for duplicate determinations in diesel and 10 $h^{-1}$ for duplicate determinations in gasoline and naphtha.

### Validation

No adequate certified reference material was available for the present work. Thus validation was performed by recovery studies and comparison with independent methods. Recoveries results for spiked As in diesel, gasoline and naphtha samples (60 µg $L^{-1}$ $n=4$) were 98±4, 99±3, and 103±5%, respectively. Concerning the comparative methods, naphtha samples were analyzed by the UOP 946–96 method [9]; gasoline and diesel samples were analyzed

**Table 4** Optimized furnace temperature programs for the determination of As in diesel, gasoline and naphtha samples stabilized as microemulsion

| | Diesel | | | Gasoline | | | Naphtha | | |
|---|---|---|---|---|---|---|---|---|---|
| Steps | Temp (°C) | Rate (°C/s) | Hold (s) | Temp (°C) | Rate (°C/s) | Hold (s) | Temp (°C) | Rate (°C/s) | Hold (s) |
| Drying | 100 | 1 | 5 | 75 | 1 | 5 | 75 | 1 | 5 |
| Drying | 200 | 1 | 5 | 150 | 2 | 3 | 150 | 2 | 3 |
| Pyrolysis | 1,008 | 100 | 15 | 947 | 100 | 25 | 1,064 | 100 | 10 |
| AZ | 1,008 | 0 | 5 | 947 | 0 | 5 | 1,064 | 0 | 5 |
| Atomize | 2,534 | FP | 3 | 2,572 | FP | 3 | 2,461 | FP | 3 |
| Cleanout | 2,650 | 1,000 | 2 | 2,650 | 1,000 | 2 | 2,600 | 1,000 | 2 |

*AZ* Auto-zero; *FP* full power

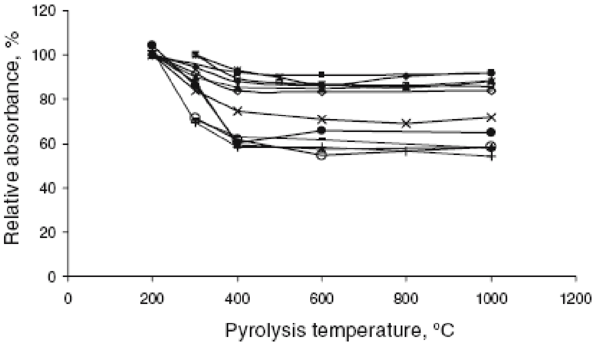


**Fig. 3** Pyrolysis temperature curves using Ir as permanent modifier and samples stabilized as microemulsions: inorganic As spiked in (*empty squares*) diesel (*filled triangles*) gasoline and (*filled squares*) naphtha; organic As spiked in (*asterisks*) diesel, (*filled diamonds*) gasoline and (*empty diamonds*) naphtha; the same experiment with 13 days incubated spiked samples: inorganic As in (*empty circles*) diesel, (+) gasoline and (*empty triangles*) naphtha; organic As in (–) diesel, (*x*) gasoline and (*filled circles*) naphtha

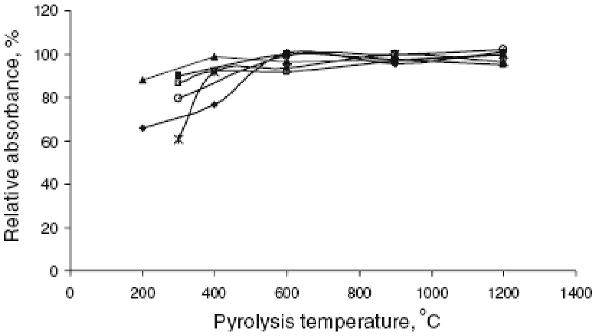


**Fig. 4** Pyrolysis temperature curves using conventional Pd modifier and samples stabilized as microemulsions: inorganic As spiked in (*empty squares*) diesel, (*filled triangles*) gasoline, (*filled squares*) naphtha and organic As spiked in (*asterisks*) diesel, (*filled diamonds*) gasoline, and (*empty circles*) naphtha

by the procedure proposed by Z. Aneva et al. [13] and EPA 3031 method [14], respectively. The results, displayed in Table 5 show an excellent agreement between developed and comparative procedures.

## Conclusions

It has been already demonstrated that sample stabilization is mandatory in the determination of some metal traces in petroleum derivates at the µg L$^{-1}$ level [1, 22, 24]. In the case of As, the present study showed that losses are observed in spiked gasoline, diesel, and naphtha samples, a point that was not addressed in most previous studies dealing with the same issue [4, 5, 15, 16]. Losses were also observed in a non-spiked gasoline sample. The performance of similar experiments with non-spiked diesel and naphtha samples led to inconclusive results due to their low As content. Excellent sample stabilization was obtained by simply mixing appropriate volumes of sample, propan-1-ol, and nitric acid aqueous solution. Prepared in the way proposed, the resulting microemulsions were spontaneously and immediately formed, leading to one-phase, transparent, and long-term stable media. This is in contrast to other emulsifying strategies that need homogenization before each measurement [17, 18], thereby limiting the use of the autosampler. Also, since no other sample pretreatment is necessary and the dilution factor is less then 2 for gasoline and naphtha and 3 for diesel, the full detection capability of the GFAAS technique could practically be exploited. The use of matrix modification proved to be necessary and the conventional Pd modifier was preferred in comparison to Ir as a permanent modifier. After multivariate optimization, As exhibited the same sensitivity in all investigated microemulsion media and in 0.2% v/v $HNO_3$ as well, making calibration with aqueous analytical solutions possible. No significant difference (Student's *t*-test, $p<0.05$) was observed between the results obtained by the proposed and independent comparative procedures. Since the contribution of the flicker noise was the main component of the total noise, the use of a more intense primary source, e.g., an EDL lamp would improve the limit of detection even further. The use of multiple injections [15, 16], or devices such as the filter furnace [11], may also improve this figure of merit.

**Table 5** Determination of As (n=3, µg L$^{-1}$) in diesel (*D*), gasoline (*G*) and naphtha (*N*) samples by the developed and comparative methods; *SD* standard deviation

| | Proposed procedure | | | | Comparative procedures[c] | |
|---|---|---|---|---|---|---|
| | Aqueous analytical calibration[a] | | Analyte addition[b] | | | |
| Samples | As | SD | As | SD | As | SD |
| D 1 | 4.7 | 0.5 | 4.8 | 0.5 | 5.0 | 0.9 |
| D 2 | <2.8 | 0.1 | – | – | <3.5 | 1.1 |
| D 3 | 4.8 | 0.3 | – | – | 4.5 | 0.7 |
| D 4 | <2.8 | 0.2 | – | – | <3.5 | 1.2 |
| D 5 | 6.6 | 0.2 | 6.1 | 0.8 | 6.2 | 1.2 |
| D 6 | 3.1 | 0.2 | – | – | <3.5 | 1.2 |
| G 1 | 5.5 | 1.3 | – | – | 5.0 | 2.6 |
| G 2 | 10.3 | 0.9 | – | – | 9.4 | 1.4 |
| G 3 | 8.9 | 0.7 | – | – | 7.1 | 2.3 |
| G 4 | 7.8 | 1.4 | 8.6 | 1.8 | 7.6 | 2.5 |
| G 5 | 8.7 | 0.3 | – | – | 8.2 | 2.4 |
| N 1 | 14.3 | 2.4 | 14.7 | 2.0 | 13.4 | 1.4 |
| N 2 | 19.0 | 1.8 | 21.1 | 1.5 | 19.2 | 1.5 |

[a] Inorganic As in 0.2% v/v $HNO_3$
[b] Microemulsion stabilized samples spiked with inorganic As
[c] As described in section Experimental

## References

1. Silva IA, Campos RC, Curtius AJ, Sella SM (1993) J Anal At Spectrom 8:749–754
2. Sithole Sd, Moyo N, Macheka M (1993) Internat J Environ Anal Chem 53:1–12
3. Carr NL, Stahlfeld DL, Robertson HG (1985) Hydrocarb Process 64:100–102
4. Botto RI (1993) J Anal At Spectrom 8:51–57
5. Hausler D (1987) Spectrochim Acta Part B 42:63–73
6. Al-Swaidan HM (1993) J Anal At Spectrosc 14:170–173
7. Kumar SJ, Gangadharan S (1999) J Anal At Spectrom 14:967–971
8. Souza RM, da Silveira CLP, Aucélio RQ (2004) Anal Sci 20:351–355
9. UOP Method 946–96 Arsenic in petroleum naphthas by HG–AAS, ASTM International, West Conshohocken PA, USA
10. Narasaki H (1985) Anal Chem 57:2481–2486
11. Anselmi A, Tittarelli P, Katskov DA (2002) Spectrochim Acta Part B 57:403–411
12. Kowalewska Z, Bulska E, Hulanicki A (1999) Spectrochim Acta Part B 54:835–843
13. Aneva Z, Iancheva M (1985) Anal Chim Acta 167:371–374
14. EPA Method 3031 (1996) Acid digestion of oils for metals. Analysis by atomic absorption or ICP spectrometry, http://www.epa.gov/epaoswer/hazwaste/test/pdfs/3031.pdf
15. Reboucas MV, Ferreira SLC, Neto BB (2005) Talanta 67:195–204
16. Reboucas MV, Ferreira SLC, Neto BDB (2003) J Anal At Spectrom 18:1267–1273
17. Aucelio RQ, Curtius AJ (2002) J Anal At Spectrom 17(3):242–247
18. Cassella RJ, Barbosa BARS, Santelli RE, Rangel AT (2004) Anal Bioanal Chem 379:66–71
19. Cassella RJ, de Sant'Ana OD, Santelli RE (2002) Spectrochim Acta Part B 57:1967–1978
20. Saint'Pierre T, Aucelio RQ, Curtius AJ (2003) Microchem J 75:59–67
21. Nakamoto Y (2000) Bunseki Kagaku 49:43–47
22. Campos RC, dos Santos HR, Grinberg P (2002) Spectrochim Acta Part B 57:15–28
23. Aucelio RQ, Doyle A, Pizzorno BS, Tristao MLB, Campos RC (2004) Microchem J 78:21–26, 2004
24. Reyes MM, Campos RC (2005) Spectrochim Acta Part B 60:1598–1603
25. Box GEP, Hunter WG, Hunter JS (1996) In: Neto BB, Scarminio IS, Bruns RE (eds) Statistics for experimenters an introduction to design, data analysis and model building, 2nd edn. Unicamp, Sao Paulo, Brazil
26. Grinberg P, Campos RC (2001) Spectrochim Acta Part B 56:1831–1843
27. Burdge JR, Mactaggart DL, Farwell SO (1999) J Chem Educ 76:434–439

# Determination of manganese in diesel, gasoline and naphtha by graphite furnace atomic absorption spectrometry using microemulsion medium for sample stabilization

Geisamanda Pedrini Brandão[a], Reinaldo Calixto de Campos[a],
Eustáquio Vinicius Ribeiro de Castro[b], Honério Coutinho de Jesus[b]

[a]Department of Chemistry, Pontifical Catholic University, Rua Marques de S. Vicente, 225, Gávea, 22453-900, Rio de Janeiro, RJ, Brazil;
[b]Department of Chemistry, Espírito Santo Federal University, Avenida Fernando Ferrari, s.n, Campus de Goiabeiras, 29000-000, Vitória, ES, Brazil

Corresponding author:
R.C. de Campos
Fax: +55-21-3527-1309
E-mail address: rccampos@rdc.puc-rio.br

## Abstract

The determination of Mn in diesel, gasoline and naphtha samples at μg $L^{-1}$ level by GFAAS, after sample stabilization in a three component medium (microemulsion) was investigated. Microemulsions were prepared by mixing appropriate volumes of sample, propan-1-ol and nitric acid aqueous solution, and a long-term homogeneous system was immediately spontaneously formed. After multivariate optimization by central composite design the optimum microemulsion composition as well as the temperature program was defined. In this way, calibration using aqueous analytical solution was possible, since the same sensitivity was observed in the optimized microemulsion medium and 0.2% v/v $HNO_3$. Recoveries at the 3 μg $L^{-}$1 level using both inorganic and organic Mn standards spiked solutions ranged from 98 to 107% and the limits of detection were 0.6, 0.5 and 0.3 μg $L^{-1}$ in the original diesel, gasoline and naphtha samples, respectively. The Mn characteristic concentration was 0.17 μg $L^{-1}$ for an injection volume of 20 μL. Typical coefficients of variation of 4, 5 and 8% were found for ten consecutive measurements at concentration levels of 0.3, 0.8, and 1.5μg $L^{-1}$, respectively. The total determination cycle lasted 4 min for diesel and 3 min for gasoline and naphtha, equivalent to a sample throughput of 7 $h^{-1}$ for duplicate determinations in diesel and 10 $h^{-1}$ for duplicate determinations in gasoline and naphtha. Accuracy was assessed by comparative analysis and no statistically significant difference was found between the results obtained with the proposed and chosen reference methods in the analysis of real samples.

*Keywords:* Manganese, diesel, gasoline, naphtha, microemulsion, GFAAS

## 1. Introduction

Information on trace element concentrations in petroleum derivatives is getting increasingly importance because of environmental and economic issues. Their presence in products such as gasoline and diesel reduces the efficiency of catalytic reactors in vehicle exhaust systems, increasing the emission of exhaust gases, and can impair the performance of the motor by the decomposition of the fuel, formation of precipitates or by promoting the corrosion of motor parts [1,2]. For naphtha, the determination of trace metals is important since they can poison the catalyst during the cracking process [3,4]. Some elements are already present in petroleum, appearing in the lighter fractions due to the co-distillation of their more volatile compounds; other trace metals can be introduced as contaminants during refining, storage and transport. Moreover, some elements can be added, normally in organic form, to improve some characteristics of the fuel. For example, manganese has been reported to occur over a wide range of concentrations as a natural trace element in crude oils [5] but it can be added as methylcyclopentadienyl manganese tricarbonyl (MMT) to gasoline as antiknock agent until at a level equivalent to 8.3 mg Mn $L^{-1}$ [6-8]. In addition, the content of potentially toxic elements must be evaluated since these elements are released to the atmosphere due to the use of petroleum derivate fuels as energy source in oil-fired power plants and automobiles [7]. MMT is used as fuel additive since the 70's of last century in substitution of the more toxic tetraethyllead. MMT is also used to reduce emissions [9]. Even though manganese is known to be an essential trace element for humans, high levels of this metal are associated to Parkinson's like diseases and attention deficiency [9,10,11]. The combustion of MMT produces manganese oxides, mainly $Mn_3O_4$ in the atmosphere [12] and it has been reported that Mn atmospherics levels about 5 $\mu$g $L^{-1}$ can cause chronic poisoning and induced pneumonia [13]. Thus, accurate quantification of Mn and other metals in fuel samples is important for production, technical use and environmental reasons.

Several analytical techniques for the determination of Mn in petroleum derivatives have been proposed: Gas chromatography (GC) associated to alternate current plasma (ACP) detection [13] or inductively coupled plasma optical emission spectrometry (ICP OES) [12]; high performance liquid chromatographic (HPLC) with diode laser atomic absorption spectrometry (DLAAS) detection [14]; solid phase microextraction (SPME) with atomic absorption spectrometry detection [15]; flame atomic absorption spectrometry (FAAS) [16,17], and inductively coupled plasma mass spectrometry (ICP-MS) using both electrothermal vaporization [18] and direct injection nebulization (DIN) [19].

Chromatographic methods are time-consuming, what impairs their use in routine analysis. Sample pre-treatments, such as SPME (as well as extraction to aqueous phase, combustion in an oxygen bomb and wet or dry ashing) are also time consuming and risks of contamination and losses due to sample manipulation are increased, although calibration may be made simpler since an aqueous final solution is obtained. FAAS makes it possible the direct analysis of hydrocarbon matrices after just a dilution with an adequate organic solvent or emulsion formation. However, aside its low sensitivity the nature of the organic medium as well as the physical chemical form (speciation) of the analyte may have a strong influence on the sensitivity causing calibration problems [16,17]. ICP techniques are sensitive and multielemental, but the introduction of organic solvents into the plasma requires special cares in order to avoid plasma extinction or carbon deposition on the sampler and skimmer cones (ICP-MS). ETV-ICP-MS shows improved transport efficiency compared with direct solution nebulization [18] and avoids matrix interference due the previous volatilization of the matrix. However, ICP-MS instrumentation due to its high acquisition and running cost is still inaccessible for many laboratories. An advantageous alternative for the determination of trace elements in petroleum fractions and distillates is the graphite furnace atomic absorption spectrometry (GF AAS). Although still a monoelemental technique, its sensitivity is adequate for most cases and a minimum sample pre-treatment is necessary [1,20,21,22]. The removal of the matrix during the pyrolysis step associated to a strict observation of the STPF rules makes it possible the accurate determination of trace metals in high organic loaded samples (such as petroleum derivatives) using aqueous calibration solutions prepared with inorganic standards [22].

However, no matter the analysis procedure chosen, sample stability must be considered, since metals dissolved in organic liquids at the $\mu g\ L^{-1}$ level are readily lost [1,4]. Thus, sample stabilization is mandatory for guaranteeing sample representativeness as well as repeatability along the analysis. Previous works [1,22,23,24,25] have shown that different trace elements were successfully stabilized in hydrocarbon liquid samples by the formation of three component solutions (microemulsions). Microemulsions are spontaneously and immediately formed after mixing their components, resulting in a one-phase, homogeneous, transparent and indefinitively stable medium, in contrast to emulsions [2,4]. Such stability dispenses any further shaking during analysis [2,4], permitting the full exploitation of the autosampler capabilities. Moreover, dilution factors are small, avoiding prohibitive impoverishment of the overall limit of detection.

Thus, the present work develops an alternative strategy for the determination of manganese in diesel, gasoline and naphtha by GFAAS, taking advantage of sample stabilization by formation of microemulsions.

## 2. Experimental

### *2.1. Instrumentation*

The Mn GFAAS measurements were performed with a model AAS 5 EA atomic absorption spectrometer (Carl Zeiss, Germany) equipped with a transversally heated graphite atomizer, a continuum source (deuterium lamp) background corrector and an AS-42 autosampler. Pin-platform graphite tubes (Analytik Jena, Jena, Germany; part number 407.A81.026) were used as atomization cell. A Mn hollow cathode lamp (Analytik Jena) operated at 6 mA and 279.5nm was used as line source. The slit was fixed at 0.2nm. All measurements were made in peak area, with a 4s integration time.

### *2.1.2. Materials, reagents, solutions and samples*

Argon 99.99 (AGA, Rio de Janeiro, Brazil) was used as protective and carrier gas. Ultra pure water, obtained from a Gehaka Master System apparatus (Gehaka, S. Paulo, Brazil) was used throughout. Analytical grade $HNO_3$ (Vetec, Rio de Janeiro, Brazil) was purified by subboiling distillation using an of PTFE subboiler apparatus (Hans Kuerner, Rosenheim, Germany). A 1000 mg $L^{-1}$ Mn stock solution was prepared by adequate dilution of a Titrisol ampoule (Merck, Darmstadt, Germany) with 0.2% v/v $HNO_3$. Aqueous calibration solutions were prepared by further convenient dilutions of this solution also with 0.2% v/v $HNO_3$. Organic calibration solutions were prepared by adequate dilution of a 100 mg $Kg^{-1}$ Mn sulfonate stock solution in oil (Spex 21 Oil standard –multi element solution, Metuchen, NJ, USA) with n-hexane (Vetec, Rio de Janeiro, Brazil). Propan-1-ol (Vetec, Rio de Janeiro, Brazil) was used for preparing the microemulsions while $Pd(NO_3)_2$ (10000 mg $L^{-1}$ Pd, Merck, Darmstadt, Germany), $IrCl_3$ (5000 mg $L^{-1}$ Ir in 10% $HNO_3$ v/v, Fluka, Buchs, Switzerland) and $Mg(NO_3)_2$ (2000 mg $L^{-1}$ Mg, Merck, Darmstadt, Germany) were used for preparing the modifiers. Carbon tetrachloride (Vetec, Rio de Janeiro, Brazil), bromine (Vetec, Rio de Janeiro, Brazil) and methyl isobutyl ketone - MIBK (Merck, Darmstadt, Germany) were used in the comparative procedure.

All the samples and solutions were handled in chapel and using gloves and masks with appropriate filter.

All plastic and glassware were washed with tap water, immersed in Extran (48h), rinsed with tap and deionized water, and immersed in 20% v/v $HNO_3$ for, at least, 24h. Before use, these materials were thoroughly rinsed with ultrapure water and oven dried at 40 $^{o}$C, avoiding any contact with metallic surfaces and dust contamination. Contamination was always checked up by a strict blank control. Commercial gasoline and diesel samples were collected in gas stations of the Vitória city (Brazil) in polyethylene bottles, and immediately brought to the laboratory. In the stability investigations (Fig 1), the experiments began as soon as the samples arrived in the laboratory. In the comparative analysis for accuracy assessment, the samples were analyzed in parallel by the proposed procedure and by the comparative procedure (*ASTM D 3831-90)* [105]. Similar cares were taken with the naphtha samples, which were supplied by local industries.

### *2.2. Procedures*

### *2.2.1. Proposed procedure*

The samples (diesel, gasoline and naphtha) were immediately stabilized after collection. The stabilization was achieved by mixing the sample with propan-1-ol and $HNO_3$ solutions at 5.9:4.0:0.1, 6.7:3.2:0.1, 6.6:3.3:0.1 volume ratios for diesel, gasoline and naphtha, respectively, and shaking manually. The $HNO_3$ concentrations were 45, 40 and 75% v/v for the three studied kind of samples, respectively. Twenty microliters of the stabilized three components sample were then injected into the graphite atomizer. Calibration was performed with aqueous (0.2% v/v $HNO_3$) calibration solutions.

### *2.2.2. Comparative procedure- ASTM D 3831-90* [105] *-modified*

To 1.0mL of the sample, 100 $\mu$L of 50% v/v bromine solution (in $CCl_4$) were added, and mixed. This solution was diluted with 2.0 mL of MIBK and 20$\mu$L were then injected in the graphite atomizer. Calibration was performed with organic calibration solutions submitted to the same treatment. The modifications in relation to the ASTM procedures were the use of GF AAS instead of F AAS and the dilution ratio (1+2 instead of 1+9 of the original procedure). These modifications were necessary for limit of detection amelioration.

## 3. Results and discussion

### *3.1. Mn stabilization in the samples*

The stability of Mn in diesel and gasoline samples *in natura* was investigated. For naphtha, the sample was spiked with both inorganic and organic Mn standards, since original levels could not be detected. The samples were transferred to autosampler cups of different materials (polyethylene, teflon and glass) and periodically analyzed, using no modifier. Although it is still not the optimized temperature program, it served for the present purpose, since only relative results are necessary. In order to avoid evaporation, the autosampler cups were closed tightly between each measurement. Manganese signal drop over time was observed in all cases (Fig 1a). In general, the drop is larger for Mn in naphtha, followed by diesel and gasoline. These drops were attributed to the adsorption of analyte traces on the containers' wall. The same test was performed with the samples stabilized by the formation of three component solutions, prepared by mixing appropriate volumes of the sample, propan-1-ol and $HNO_3$ aqueous solution, forming a microemulsion: No

Mn signal drop was observed over several days in any situation, proving the long-term stabilization of the three types of samples (Fig 1b). The volume proportions of the microemulsions are as described in section 2.2.1, and their respective optimization is shown in section 3.3.

### 3.2. Matrix modifiers

The necessity and performance of conventional (Pd, Mg or Pd/Mg) and permanent (Ir) modifiers were evaluated by pyrolysis temperature curves, using samples stabilized as microemulsion. Non-spiked gasoline and diesel samples were used. The naphtha sample was spiked (2 µg $L^{-1}$) with organic Mn before stabilization, since its original Mn content was too low for the present study. An aqueous analytical solution (3 µg $L^{-1}$) was also investigated. For gasoline, naphtha and the aqueous solution the conventional modifier solution volume was 10µL. Their concentrations were 1000, 1000 and 500+500 mg $L^{-1}$ for the Pd, Mg and Pd+Mg modifiers solutions, respectively. Since the modifier solution is aqueous and the sample is stabilized as microemulsion, if both are mixed, the microemulsion breaks, and interaction fails. Thus, the modifier solutions were dried before the sample addition onto the platform aiming at permitting a better interaction between the modifier and the sample. In the investigation of the permanent modifier, a total of 600µg of Ir was deposited onto the graphite platform using the coating procedure described by Grinberg *et al* [27]. For aqueous solution using the studied conventional modifiers, higher pyrolysis temperatures can be used in comparison to the solution without a modifier; however, the modifiers resulted in a significant loss of sensitivity, which might be due to an over-stabilization effect. The Ir permanent modifier has not improved the pyrolysis temperatures as well as resulted in the worst sensitivity. In general, the same trend was observed for diesel, gasoline and naphtha samples stabilized as microemulsion. Since only low background attenuation was observed at the maximum allowed pyrolysis temperature without modifier, and no evident advantage was foreseen by their use by the present study, further experiments were carried out without modifier.

### *3.3. Multivariate optimization of the microemulsion composition and temperature program*

The optimization of the microemulsion composition (proportion) as well as the graphite furnace temperature program for each kind of sample was performed by multivariate optimization. The variables related to the microemulsion composition were the nitric acid final concentration and the sample/propan-1-ol volume ratio. The $HNO_3$ solution volume and microemulsion total volume were kept constant at 100µL and 10mL, respectively. The pyrolysis and atomization temperatures were the variables related to the furnace temperature program. In principle, a complete factorial design ($2^4$) was performed, with 4 factors and 2 levels. The 16 ($2^4$) experiments were made at a random order. The data were analyzed by using the Statistica 6.0 Statsoft software and the $2^{(k-p)}$ standard design [28]. This design delivers a linear model, for which the F test showed lack of fit, and the low $R^2$ values for all samples indicated that the linear model obtained was not adequate. Thus, the factors were optimized by a central composite design, performing 16 ($2^4$) experiments related to the factorial design, 8 (2x4) star experiments ($\alpha = \pm 16^{1/4}$) and 5 central experiments. The different levels are shown in Table 1. The central values were taken from the previous experiments concerning the pyrolysis temperature curves without modifier. The Table 2 show the regression coefficients of the significant effects ($p<0.05$) for each kind of sample. The $R^2$ adjusted values were 0.824, 0.803 and 0.730 for Mn in diesel, gasoline and naphtha, respectively. The critical points are shown in Table 3. The optimized furnace temperature programs are shown in Table 4. The other steps of the temperature program were set in accordance to previous experience with similar samples [1,22,25]. Drying temperatures and rates were visually optimized, so to permit a complete evaporation of the solvent, without sample ejection, at a minimum time. Pyrolysis ramp rate were optimized considering the elimination of small explosions that occur if a too fast ramp is used. Atomization ramp was optimized considering the signal shape, that is, a signal resolution within an integration time of 4s. Note that for the diesel samples a slower drying ramp was necessary as well as a higher drying temperature [22,25].

### 3.4. Calibration

Aqueous calibration curve (0.2% $HNO_3$ v/v) was compared with calibration curves derived from spiking low Mn level samples (stabilized as microemulsion) with both inorganic and organic Mn. Inorganic Mn was dissolved in propan-1-ol and organic Mn in n-hexane. The curves' slopes and the correlation coefficients ($R^2$) obtained were: spiked inorganic Mn in 0.2% v/v $HNO_3$ aqueous solution [$y=0.033x$ (±0.001); $R^2=0.9987$] and in microemulsion media of diesel [$y=0.031x$ (±0.001); $R^2=0.9969$], of gasoline [$y=0.031x$ (±0.001); $R^2=0.9981$] and of naphtha [$y=0.032x$ (±0.001); $R^2=0.9977$]; spiked organic Mn in microemulsion media of diesel [$y=0.031x$ (±0.001); $R^2=0.9939$], of gasoline [$y=0.030x$ (±0.001); $R^2=0.9979$] and of naphtha [$y=0.033x$ (±0.001); $R^2=0.9986$]. Thus, no significant difference (Student-t test, $p<0.05$) was observed for the curves' slopes. That is, the same sensitivity was observed in all cases, supporting the adequacy of calibration with aqueous calibration solutions.

### 3.5. Analytical figures of merit

The limits of detection (LOD) at the optimized conditions were 0.6, 0.5 and 0.3 µg $L^{-1}$ in the original diesel, gasoline and naphtha samples, respectively, calculated according the IUPAC: Three times the standard deviation for 10 measurements of the microemulsion blank, divided by the slope of the calibration curve, multiplied by the sample dilution factor. In this case, the microemulsion blanks were obtained using real samples with Mn levels below the LOD. The differences of LOD are due to different accuracies for each kind of matrix. The Mn characteristic concentration was 0.17 µg $L^{-1}$ for an injection volume of 20 µL. The total determination cycle lasted 3 min for gasoline and naphtha and 4 min for diesel, equivalent to sample throughputs of 10 $h^{-1}$ for duplicate determinations in gasoline and naphtha and 7 $h^{-1}$ for duplicate determinations in diesel.

### 3.6. Accuracy

Since there is no adequate certified reference material for the present investigation, accuracy was first assessed by recovery tests. Samples (stabilized as microemulsions) were spiked with both inorganic Mn (3 µg $L^{-1}$, n = 4) as well as with organic Mn (~3 µg $L^{-1}$, n = 4). In the tests with inorganic Mn, the recoveries were 98 ± 4, 98 ± 1 and 98 ± 4 %, for diesel, gasoline and naphtha samples, respectively. In relation to the organic Mn spiked samples these figures were 107 ± 3, 96 ± 1 and 105 ± 5 %. Accuracy was further assured by the Mn determination in diesel, gasoline and naphtha samples using the proposed and a comparative procedure (*ASTM D 3831-90)* [105], modified as described is section 2.2.2.. It was used an ASTM method, even modified, since it is a known and well established method, though the LOD limitation. The use of another method with a lower LOD would imply in the validation of this method, and would fall in a recurrent problem, out of the scope of the present work. The gasoline and diesel samples were collected in gas stations of the Vitória city (Brazil) and the naphtha samples were supplied by local industries. The results are shown in Table 5, where no significant difference between the results arisen from both procedures is observed (ANOVA, univariate). It is worth mentioning that Brazilian gasoline does not contain manganese as MMT, using ethanol (20-24% v/v) as antiknock agent.

## 4. Conclusions

Sample stabilization showed to be mandatory for the determination of Mn at the low µg $L^{-1}$ level in the studied samples. This is of concern not only during analysis but specially for defining sampling and storage strategies, no matter the analytical method employed. Otherwise, sample representativeness will be lost and the analysis turns senseless. Excellent sample stabilization was obtained by simply mixing appropriate volumes of the samples, propan-1-ol and nitric acid aqueous solution, resulting in one-phase, transparent and long term stable media. This is in contrast to other emulsifying strategies that need mechanical homogenization before each measurement, limiting the use of the autosampler. Also, no sonication assistance is necessary, turning the procedure adequate for field use. Since no other sample pre-treatment is necessary and the dilution factor is less then 2, practically the full detection capability of the GF AAS could be exploited. The use of matrix modification (Pd, Mg, Pd/Mg and Ir) was unnecessary and background attenuation was always within the range of the background correction system. After multivariate optimization Mn exhibited the same sensitivity in all investigated media (including aqueous). In consequence, calibration with aqueous calibration solutions was possible. Thus, the main advantages of the proposed procedure are: the lower dilution factor, resulting in better LOD; the microemulsion is formed easily and stabilizes the sample. Besides, the use of organic standards for calibration is not necessary: The calibration can be performed with aqueous calibration solutions, using less expensive and more available aqueous standard solutions. Furthermore, the use aggressive reagents and organic solvents are avoided. The use of multiple injections [29,30] or devices such as the filter furnace [20] may improve the limit of detection even further.

## 5. References

1. I.A. Silva, R.C. Campos, A.J. Curtius, S.M. Sella, Determination of lead and copper in kerosene by electrothermal atomic absorption spectrometry: stabilization of metals in organic media by a three-component solution, *J. Anal. At. Spectrom.* 8 (1993) 749-754.
2. R.Q. Aucelio, A.J. Curtius, Evaluation of electrothermal atomic absorption spectrometry for trace determination of Sb, As and Se in gasoline and kerosene using microemulsion sample introduction and two approaches for chemical modification, *J. Anal. At. Spectrom.*, 17 (2002) 242-247.
3. S.J. Kumar, S. Gangadharan, Determination of trace elements in naphtha by inductively coupled plasma mass spectrometry using water-in-oil emulsions, *J. Anal. At. Spectrom.*, 14 (1999) 967–971.
4. R.J. Cassella, B.A.R.S. Barbosa, R.E. Santelli, A.T. Rangel, Direct determination of arsenic and antimony in naphtha by electrothermal atomic

absorption spectrometry with microemulsion sample introduction and iridium permanent modifier, *Anal. Bioanal. Chem.*, 379 (2004) 66-71.

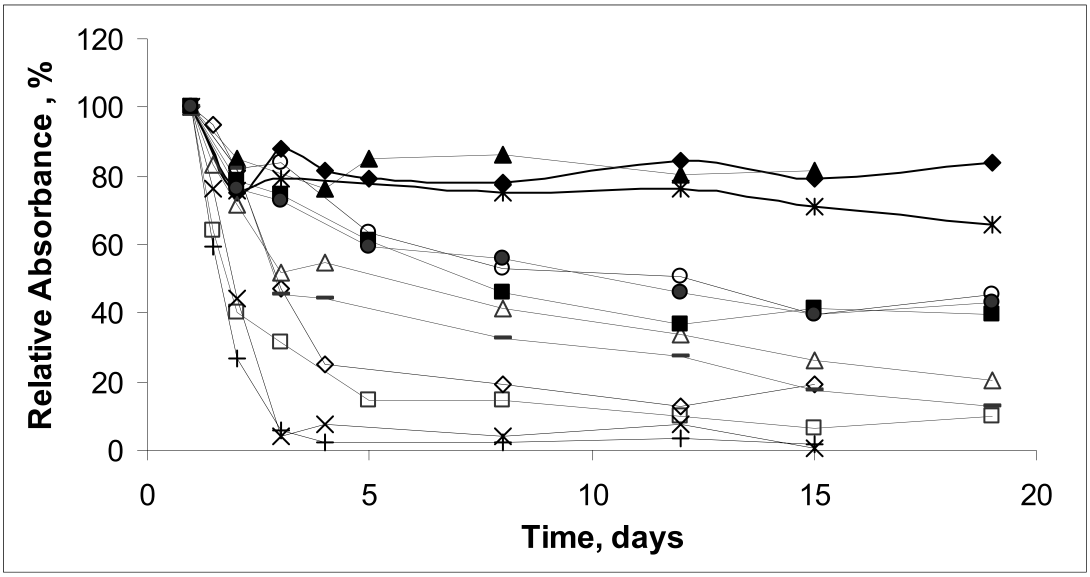
5. W.K. Robbins, Analysis of petroleum for trace-metals - Determination of trace quantities of manganese in petroleum and petroleum-products by heated vaporization atomic-absorption, *Anal. Chem.*, 46 (1974) 2177-2182.
6. Q. Wei, B. Du, Rapid and selective method for the spectrophotometric determination of nickel naphthenate in gasoline in a microemulsion, *Talanta*, 45 (1998) 957-961.
7. B. Gulson, K. Mizon, A. Taylor, M. Korsch, J. Stauber, J.M. Davis, H. Louie, M. Wu, H. Swan, Changes in manganese and lead in the environment and young children associated with the introduction of methylcyclopentadienyl manganese tricarbonyl in gasoline - preliminary results, *Environ. Res.*, 100 (2006) 100-114.
8. Gasoline Additive MMT, , U.S. EPA, http://www.epa.gov/otaq/regs/fuels/additive/mmt_cmts.htm, Washington, D.C. (2007)
9. D.J. Butcher, Speciation of methylcyclopentadienyl manganese tricarbonyl and its derivatives: A review *Appl. Spectros. Rev.*, 37 (2002) 1-17.
10. Manganese, U.S. EPA, http://www.epa.gov/iris/subst/0373.html, Washington, D.C. (1996).
11. B. Hileman, The environment and Parkinson's, *Chem. & Engineer. News*, 79 (2001) 35-37.
12. H.B. Swan, Speciation and quantification of organic manganese compounds in gasoline by gas chromatography atomic emission spectroscopy, *Bull. Environ. Contam. Toxicol.*, 63 (1999) 491-498.
13. J.M. Ombaba, E.F. Barry, Determination of (methylcyclopentadienyl) manganesetricarbonyl in gasoline by capillary gas-chromatography with alternating-current plasma emission detection, *J. of Chromatography A*, 678 (1994) 319-325.
14. D.J. Butcher, A. Zybin, M.A. Bolshov, K.Niemax, Speciation of methylcyclopentadienyl manganese tricarbonyl by high-performance liquid

chromatography-diode laser atomic absorption spectrometry, *Anal. Chem.*, 71 (1999) 5379-5385.

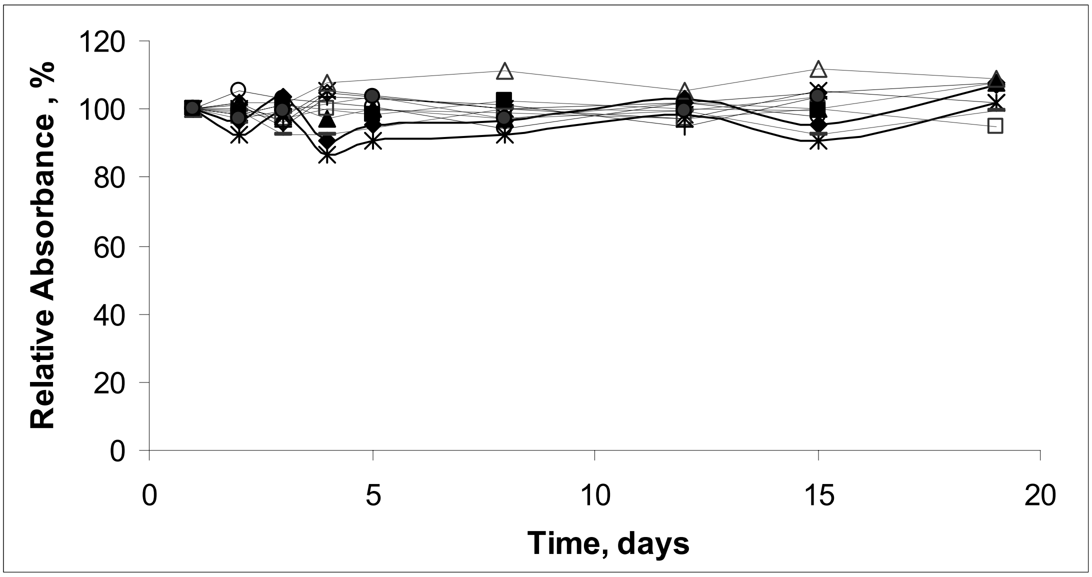
15. M.S. Fragueiro, F. Alava-Moreno, I. Lavilla, C. Bendicho, Determination of methylcyclopentadienyl-manganese tricarbonyl by solid phase microextraction-direct thermal desorption-quartz furnace atomic absorption spectrometry, *Spectrochim. Acta Part B*, 56 (2001) 215-221.
16. R.J. Lukasiewicz, B.E. Buell, Direct determination of manganese in gasoline by atomic-absorption spectrometry in nitrous oxide hydrogen flame, *Appl. Spectrosc.*, 31 (1977) 541-547.
17. B. Du, Q. Wei, G. Xu, Rapid determination of methylcyclopentadienyl manganese tricarbonyl in gasoline by FAAS, *Anal. Letters*, 32 (1999) 1011-1021.
18. T.D. Saint'Pierre, L.F. Dias, D. Pozebon, R.Q. Aucelio , A.J. Curtius, B. Welz, Determination of Cu, Mn, Ni and Sn in gasoline by electrothermal vaporization inductively coupled plasma mass spectrometry, and emulsion sample introduction, *Spectrochim. Acta Part B*, 57 (2002) 1991-2001.
19. R.I. Botto, Trace element analysis of petroleum naphthas and tars using direct injection ICP-MS, *Canadian J. of Anal. Sci. and Spectrosc.*, 47 (2002) 1-13.
20. A. Anselmi, P. Tittarelli, D.A. Katskov, Determination of trace elements in automotive fuels by filter furnace atomic absorption spectrometry, *Spectrochim. Acta Part B*, 57 (2002) 403-411.
21. Z. Kowalewska, E. Bulska, A. Hulanicki, Organic palladium and palladium-magnesium chemical modifiers in direct determination of lead in fractions from distillation of crude oil by electrothermal atomic absorption analysis, *Spectrochim. Acta Part B*, 54 (1999) 835-843.
22. G.P. Brandão, R.C. Campos, A.S. Luna, E.V.R. Castro, H.C. Jesus, Determination of arsenic in diesel, gasoline and naphtha by graphite furnace atomic absorption spectrometry using microemulsion medium for sample stabilization, *Anal. Bioanal. Chem.*, 385 (2006) 1562-1569.
23. R.C. de Campos, H.R. dos Santos, P. Grinberg, Determination of copper, iron, lead and nickel in gasoline by electrothermal atomic absorption spectrometry using threecomponent solutions, *Spectrochim. Acta Part B*, 57 (2002)15-28.

24. R.Q. Aucelio, A. Doyle, B.S. Pizzorno, M.L.B. Tristao, R.C. Campos, Electrothermal atomic absorption spectrometric method for the determination of vanadium in diesel and asphaltene prepared as detergentless microemulsions, *Microchem. J.*, 78 (2004) 21-26.
25. M.M. Reyes, R.C. Campos, Graphite furnace atomic absorption spectrometric determination of Ni and Pb in diesel and gasoline samples stabilized as microemulsion using conventional and permanent modifiers, *Spectrochim. Acta Part B*, 60 (2005) 615-624.
26. ASTM D 3831-90: Standard Test Method for manganese in gasoline by Atomic Absorption Spectroscopy (1990).
27. P. Grinberg, R.C. Campos, Iridium as permanent modifier in the determination of lead in whole blood and urine by electrothermal atomic absorption spectrometry, *Spectrochim. Acta Part B*, 56 (2001) 1831-1843.
28. G.E.P. Box, W.G. Hunter, J.S. Hunter, Statistics for experimenters An introduction to design, data analysis and model building, in: B.B. Neto, I.S. Scarminio, R.E. Bruns, second ed., Unicamp, S. Paulo - Brazil, 1996.
29. M.V. Rebouças, S.L.C. Ferreira, B.B. Neto, Behaviour of chemical modifiers in the determination of arsenic by electrothermal atomic absorption spectrometry in petroleum products, *Talanta*, 67 (2005) 195-204.
30. M.V. Reboucas, S.L.C. Ferreira, B.D.B. Neto, Arsenic determination in naphtha by electrothermal atomic absorption spectrometry after preconcentration using multiple injections, *J. Anal. At. Spectrom.*, 18 (2003) 1267-1273.

**Figure**



(a)



(b)

Fig 1: Stability of Mn in the samples (a) *in natura* or (b) stabilized as microemulsion, stored in: polyethylene cups: (■) diesel, (♦) gasoline; (□) naphtha spiked with inorganic Mn and (+) naphtha spiked with organic Mn; teflon cups: (○) diesel, (▲) gasoline; (x) naphtha spiked with inorganic Mn and (-) naphtha spiked with organic Mn; glass cups: (●) diesel; (∗) gasoline and (◊) naphtha spiked with inorganic Mn and (Δ) naphtha spiked with organic Mn.

## Tables

Table 1: Studied variables and their respective levels for the central composite design.

| Variable | Levels | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Diesel | | | | | Gasoline | | | | | Naphtha | | | | |
| | -2 | -1 | 0 | +1 | +2 | -2 | -1 | 0 | +1 | +2 | -2 | -1 | 0 | +1 | +2 |
| Pyrolysis temperature (ºC) | 500 | 700 | 900 | 1100 | 1300 | 800 | 900 | 1000 | 1100 | 1200 | 800 | 900 | 1000 | 1100 | 1200 |
| Atomization temperature (ºC) | 2225 | 2300 | 2375 | 2450 | 2525 | 2225 | 2300 | 2375 | 2450 | 2525 | 2225 | 2300 | 2375 | 2450 | 2525 |
| $HNO_3$ conc (% v/v) in the microemulsion | 0.15 | 0.30 | 0.45 | 0.60 | 0.75 | 0.15 | 0.30 | 0.45 | 0.60 | 0.75 | 0.15 | 0.30 | 0.45 | 0.60 | 0.75 |
| Sample/ propan-1-ol volume ratio | 0.30 | 0.70 | 1.11 | 1.51 | 1.91 | 0.72 | 1.06 | 1.41 | 1.75 | 2.10 | 0.72 | 1.06 | 1.41 | 1.75 | 2.10 |

Table 2: Regression coefficients of the studied factors derived from the central composite design.

| Sample | Regression coefficients(1) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Interc. | $Tp^2$ | $Ta^2$ | $HNO_3^2$ | $(s/p)^2$ | Tp | Ta | $HNO_3$ | s/p | Tp.Ta | $Tp.HNO_3$ | Tp.s/p | $Ta.HNO_3$ |
| Diesel | 14.645 | -0.167 | -0.489 | -0.332 | -0.358 | 0.287 | 0.904 | ns | 0.410 | ns | ns | ns | ns |
| Gasoline | 3.854 | -0.059 | -0.084 | -0.041 | ns | -0.061 | -0.130 | ns | -0.243 | 0.063 | ns | -0.051 | 0.049 |
| Naphtha | 15.578 | ns | ns | ns | 0.099 | Ns | -0.425 | -0.212 | -0.317 | ns | ns | ns | 0.166 |

(1) Interc., Tp, Ta, $HNO_3$, s/p and ns refer to intercept, pyrolysis temperature, atomization temperature, $HNO_3$ solution concentration, sample/propan-1-ol volume ratios, and “non significant”, respectively.

Table 3: Critical (optimum) points for the studied variables after the central composite design optimization.

| Variable | Critical values | | |
|---|---|---|---|
| | Diesel | Gasoline | Naphtha |
| Pyrolysis temperature (ºC) | 1100 | 800 | 950 |
| Atomization temperature (ºC) | 2450 | 2300 | 2430 |
| $HNO_3$ conc. in the microemulsion (% v/v) | 0.45 | 0.40 | 0.75 |
| Sample / propan-1-ol volume ratio | 1.47 | 2.10 | 2.00 |

Table 4: Optimized temperature programs for the determination of Mn in diesel, gasoline and naphtha samples stabilized as microemulsion.

| | Diesel | | | Gasoline | | | Naphtha | | |
|---|---|---|---|---|---|---|---|---|---|
| Step | Temp (ºC) | Rate (ºC/s) | Hold (s) | Temp (ºC) | Rate (ºC/s) | Hold (s) | Temp (ºC) | Rate (ºC/s) | Hold (s) |
| Drying | 100 | 5 | 5 | 100 | 5 | 5 | 100 | 5 | 5 |
| Drying | 180 | 2 | 10 | 200 | 3 | 10 | 200 | 3 | 10 |
| Drying | 250 | 1 | 5 | - | - | - | - | - | - |
| Pyrolysis | 1100 | 100 | 20 | 800 | 100 | 20 | 950 | 100 | 20 |
| AZ(1) | 1100 | 0 | 5 | 800 | 0 | 5 | 950 | 0 | 5 |
| Atomize | 2450 | 2000 | 3 | 2300 | 2000 | 3 | 2430 | 2000 | 3 |
| Cleanout | 2600 | 500 | 2 | 2550 | 500 | 2 | 2550 | 500 | 2 |

Table 5: Determination of Mn (n=3, $\mu$g L$^{-1}$) in gasoline (G), diesel (D), and naphtha$^{(1)}$ (N) samples by the proposed and comparative procedures.

| Sample | Proposed procedure | | ASTM D 3831-90 | |
|---|---|---|---|---|
| | Mn | sd $^{(2)}$ | Mn | sd $^{(2)}$ |
| G1 | 1.3 | 0.1 | 1.5 | 0.3 |
| G2 | 1.2 | 0.2 | 0.8 | 0.4 |
| G3 | 1.6 | 0.4 | 2.4 | 0.5 |
| G4 | 2.9 | 0.4 | 2.1 | 0.5 |
| G5 | 1.1 | 0.2 | 1.7 | 0.4 |
| G6 | 0.9 | 0.3 | 1.6 | 0.5 |
| D1 | 1.5 | 0.2 | 1.4 | 0.2 |
| D2 | 0.6 | 0.2 | 0.4 | 0.3 |
| D3 | 1.4 | 0.3 | 0.9 | 0.4 |
| D4 | 1.2 | 0.2 | 1.7 | 0.2 |
| N1 + 1.0 | 1.2 | 0.2 | 1.5 | 0.3 |
| N1 + 2.0 | 2.1 | 0.1 | 2.2 | 0.3 |
| N1 + 3.0 | 3.1 | 0.2 | 2.4 | 0.3 |
| N2 + 1.5 | 1.6 | 0.1 | 1.4 | 0.2 |

(1) Mn in naphta samples was below the LOD; the samples were then spiked with organic Mn, attaining the concentration values (in µg L$^{-1}$) displayed in the respective cell.

(2) sd = standard deviation.