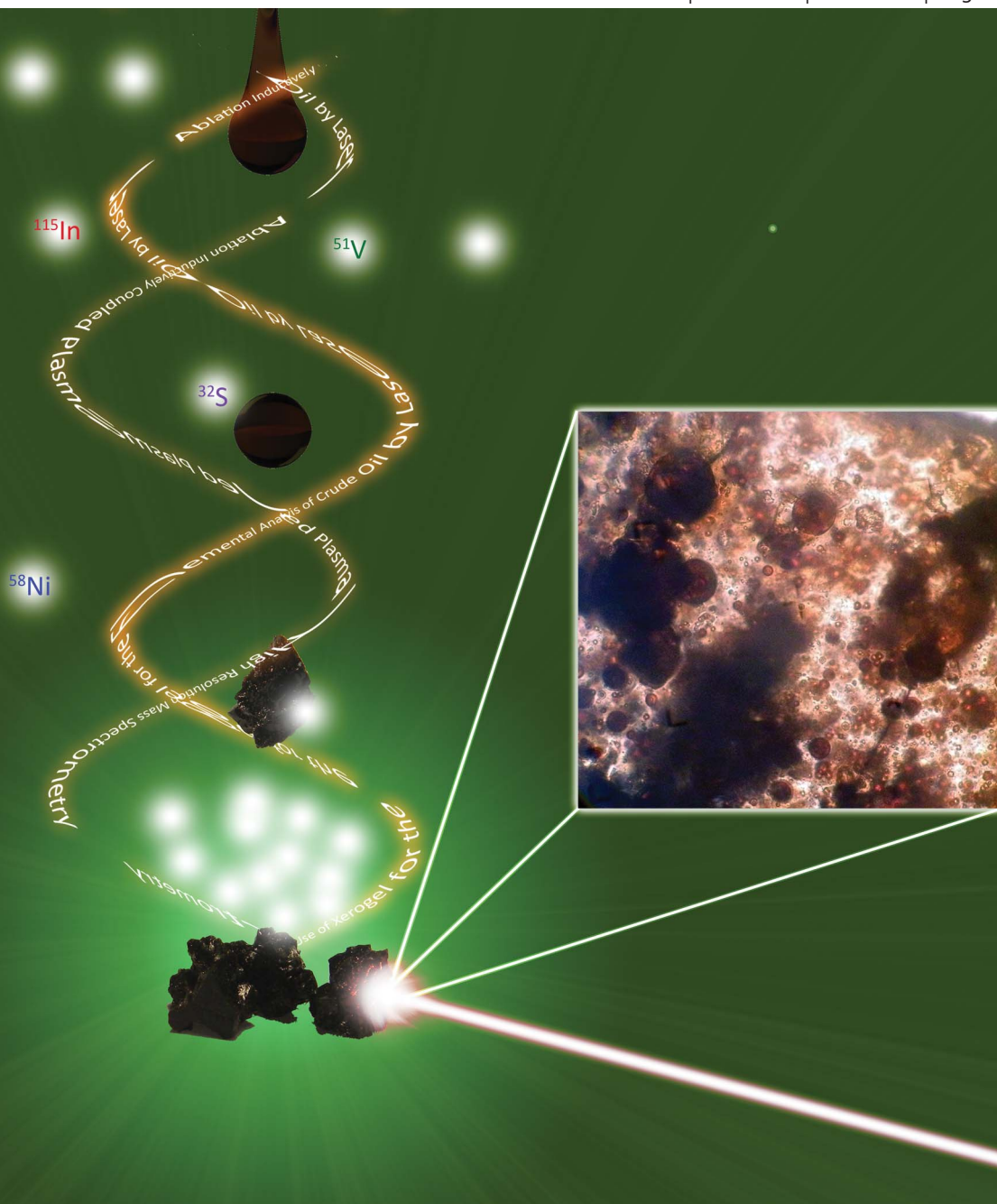


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Use of xerogels for the elemental analysis of crude oils by laser ablation inductively coupled plasma high resolution mass spectrometry

Mauro Martínez,^a Carine Arnaudguilhem,^b Ryszard Lobinski,^b Brice Bouysiere,^b Manuel Caetano^a and José Chirinos^{*a}

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A novel method for the preparation of crude oil samples based on a xerogel matrix was developed for elemental analysis using laser ablation–double focusing sector field inductively coupled plasma–mass spectrometry. The samples and aqueous solution were successfully encapsulated using zirconium *n*-propoxide. The use of xerogel produces stable and homogeneous pellets, avoids splashing of the sample and allows the use of aqueous inorganic standards to elaborate the calibration curve. Sulfur, nickel and vanadium were selected as test elements and indium was used as the internal standard to correct the variations in the amount of material ablated. The correlation coefficients of the calibration curves for all the elements tested were better than 0.990 except for sulfur. Crude oil results showed no significant statistical differences between the sol–gel results and those obtained with similar studies.

Introduction

Inductively coupled plasma mass spectrometry (ICP MS) and inductively coupled plasma optical emission spectrometry (ICP OES) have been established as the principal techniques for the analysis of petroleum products thanks to their multielement capability and analytical figures of merits.^{1–14} Several methods have been reported to analyze crude oils and their derivatives. The traditional ones consist of the sample digestion under strong oxidative conditions, usually microwave-assisted.^{2–5} These methods reduce interferences and avoid all the organic matrix analyses by ICP MS with the inconvenience of being time consuming and prone to alter the concentration of the analytes. The preferred procedures involve the dilution of the sample in organic solvents that are simple, can be automated and are less time consuming.^{2–4} However, the introduction of organic solvents into the plasma may produce overloading of the plasma and the addition of oxygen in the plasma is necessary in order to reduce carbon deposition on the sampler and skimmer cones. Different strategies have been satisfactorily reported to deal with volatile organic effects: μ -flow injection,^{6,7} emulsification techniques^{8,9} and discrete microsampling techniques such as electrothermal vaporization and laser ablation (LA).^{10–14}

The analysis of petroleum samples based on LA is very attractive from the analytical point of view because it allows the direct introduction of the sample without the inconvenience produced by traditional pretreatment methods.^{10–14} However, the sample

splashing and the selection of the accurate calibration technique, mainly due to the absence of the appropriate standards, are the major limitation. Diverse methods have been reported for the treatment of petroleum samples in LA-ICP or LIBS: use of powders compacted by fusion or by pelletization,¹⁰ use of dried aerosol produced by ultrasonic nebulization with the standard addition method,¹¹ isotope dilution quantification with the use of petroleum impregnated cellulose,¹² the use of silica gel plates¹³ and the development of internal glass cap to fit into the ablation cell.¹⁴

The fusion of powders is the simplest procedure and leads to the formation of ideally homogeneous targets but requires the use of high temperatures which may cause vaporization of volatile elements. Pelletization presents inconvenience with homogeneity and target cohesion. Recently, the use of sol–gel matrices for the preparation of standards for the analysis of diverse samples in LA has been reported.^{15–21} The sol–gel process allows for formation of glassy and ceramic materials in temperatures much lower than those offered by conventional melting techniques. The technology of sol–gel offers some analytical advantages when compared to conventional glass: the whole process can be performed at room temperature and the glass is obtained from the liquid precursors.¹⁵ The preparation of sol–gels involves the evolution of inorganic network, formation of colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel). Drying of the obtained gel, even at room temperatures, produces glass-like materials called xerogels (xeros-dry). This process allows us to add various chemical substances (as a solution, suspension or solid samples) to the hydrolyzate and after the gelation step, to entrap them within the gel. Methodologies for the successful analysis of biological tissue, soils, coal and minerals have been reported.^{16–20}

^aEscuela de Química, Facultad de Ciencias, Universidad Central de Venezuela, P.O. box 47102, Caracas 1041a, Venezuela. E-mail: jose.chirinos@ciens.ucv.ve; Fax: +58 212 6934977; Tel: +58 212 6051174

^bCNRS-UPPA, UMR 5254, LCABIE, Hélioparc, 2av. Pr. Angot, 64053 Pau, France

For all above mentioned, the aim of this work is to optimize a procedure to encapsulate crude oil samples in a xerogel matrix to be used in laser ablation double focusing sector field inductively coupled plasma mass spectrometry (LA-ICP-SFMS) analysis. To the best of our knowledge, this is the first attempt to encapsulate a crude oil sample. The latter is difficult to encapsulate mainly because it is not soluble in the aqueous media generally used to produce sol–gels. The idea of this work is to produce homogeneous xerogels that avoid splashing effects of the crude oils and evaluates the possibility to employ aqueous inorganic solutions to elaborate the calibration curves. Sulfur, nickel and vanadium were used as tested elements and the results were compared to similar studies that analyze crude oil samples using LA-ICP-SFMS.

Experimental

Instrument

A double-focusing sector-field (ICP-SFMS) instrument (Element XR, Thermo Fisher Scientific, Bremen, Germany) was used. It was equipped with a Fassel-type quartz torch shielded with a grounded Pt electrode and a quartz bonnet. A standard quartz injector (1.75 mm i.d.) was used.

A New Wave Research (Fremont, CA) UP-213 Nd:YAG system was used for LA. The laser provided flat craters by a “resonator-flat” beam. An ablation chamber was mounted on a three-axis translation stage and coupled to the ICP torch using a 60 cm Tygon tube (5.0 mm i.d.). The ablated material was swept by helium carrier gas and mixed with an argon makeup gas of the spectrometer prior to introduction into the plasma. Ni sampler (orifice diameter 1.1 mm) and skimmer (orifice diameter 0.8 mm) cones were utilized. Typical operating LA-ICP-MS conditions are given in Table 1.

Reagents and samples

Xerogels were obtained by using Zirconium *n*-propoxide (TPOZ) (70% in 1-propanol, Aldrich), trace metal grade methanol (Anachemia), anhydrous ethanol, high-purity concentrated nitric acid (Anachemia), and Tergitol® solution (70% nonylphenol ethoxylate in H₂O, Aldrich). Aqueous S, V, Ni and In solutions used to elaborate the calibration curves were prepared from 1000 µg mL⁻¹ standard stock solutions (spectrometric grade, SCP Science). Crude oils having different American Petroleum Institute (API) gravities from different countries were used as test samples.

Results and discussion

Optimization of the xerogels preparation

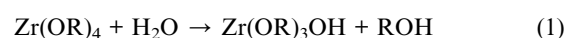
A xerogel derived oxide matrix is an amorphous solid prepared *via* sol–gel processing, in which a colloidal suspension (sol) is first formed by mixing liquid metal (*e.g.*, zirconium *n*-propoxide, TPOZ) or silicon (*e.g.*, tetraethoxysilane, TEOS) alkoxide precursors, water, a co-solvent, and an acid or base catalyst. Alkoxy groups are removed by acid- or base-catalysed hydrolysis reactions (eqn (1)), and networks of M–O–M–O linkages (gel) are formed in subsequent condensation reactions, which can

Table 1 Compromised working parameters set to LA-ICP-SFMS

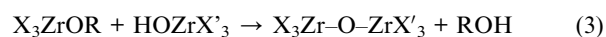
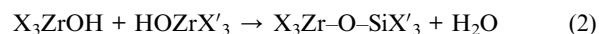
Thermo Fisher Scientific Element XR ICP MS	
<i>ICP ion source and ion transmission</i>	
Forward power/W	1500
Plasma Ar gas flow rate/L min ⁻¹	16.00
Auxiliary Ar gas flow rate/L min ⁻¹	0.90
Make-up Ar gas flow rate/L min ⁻¹	0.70
Extraction lens/V	–2000
Focus lens/V	–1200
X-Deflection lens/V	–1.50
Y-Deflection lens/V	–3.00
Shape lens/V	130
SEM potential/V	2800
<i>Data acquisition</i>	
Measured isotope	⁶⁰ Ni, ¹¹⁵ In, ³² S, ⁵¹ V
Search and integration window (%)	60
Settling time/ms	1 (⁶⁰ Ni, ³² S), 34 (⁵¹ V)
Sampling time/ms	10 (³² S), 50 (⁶⁰ Ni, ⁵¹ V)
Number of samples per peak	20
Detection mode	Triple
Scan type	E-scan
Integration type	Average
Mass resolution	4000 (medium)
New Wave Research UP-213 LA	
Wavelength/nm	213
Pulse energy/mJ	0.45 (50%)
Fluence/J cm ⁻²	1.43
Spot size/µm	200
Repetition rate/Hz	20
Scan speed/µm s ⁻¹	40
Carrier He gas flow rate/L min ⁻¹	0.50

produce either water or alcohol as shown in eqn (2) and (3), involving hydroxyl groups.

Hydrolysis:



Condensation:



The pH value influences the rate of reaction and thereby the time necessary for gel formation. The zirconium gel time is longest at the isoelectric point at pH 2.2 and rapidly decreases under acid or base conditions relative to the isoelectric point pH 2.2.

There are numerous literature references that deal with different procedures for the synthesis of sol–gel materials.^{16–20} However, in the case of the crude oil samples and their standards, it was necessary to optimize the preparation procedures. Crude oils are not soluble in the aqueous media used to produce sol–gels and they are not efficiently trapped. For this reason, dissolution of the sample, in dichloromethane and methanol, was used to get homogeneous xerogels. Fig. 1 presents a schematic diagram of the xerogel preparation. The crude oils were encapsulated using the following optimized method: 0.5000 g of the crude oil was dissolved in dichloromethane and added to the TPOZ, and after that this mixture was added to the other reagents. The resulting xerogels were dried overnight in an oven at 100 °C. The use of

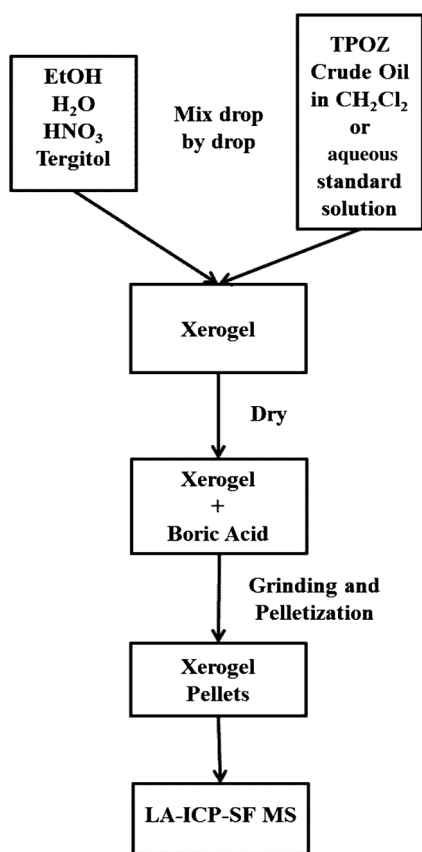


Fig. 1 Schematic diagram of the xerogel preparation.

lower temperatures can be used in the case of volatile compounds determination. However, the use of temperatures higher than 500 °C is not recommended because it can create bubbles which can explode and crack the xerogel. Prior to pelletization, the sol-gel samples were ground with a mortar. A 0.05 g sample of boric acid was then added to 0.45 g of each sample, and the resulting mixtures were homogenized for 2 min using polystyrene vials (Spex Certi-Prep, 6133) and metacrylate balls (Spex Certi-Prep, 3112) along with a grinder mixer (Spex Mixer/Mill, 5100), before final pelletization in a 13 mm die (Macro/Micro KBr die, 0012-2477) at 10 000 lb for 5 min.

The method to encapsulate aqueous inorganic standards allows stable homogeneous targets to be obtained. To a clean disposable scintillation vial (20 mL, Sarstedt) were added in the following order: 6 mL of ethanol, 50 µL of concentrated HNO₃, 20 µL of 2% from Tergitol solution, suitable quantities of a 1000 µg mL⁻¹ S, V and Ni standard solution to obtain concentrations between 0 µg g⁻¹ and 50 µg g⁻¹, 250 µL of a 1000 µg mL⁻¹ In standard solution, and 0.3 mL of deionized water. After 5 min of ultrasonic stirring, 1.8 mL of zirconium propoxide was added dropwise. Formation of a white gel is observed as soon as the alkoxide comes into contact with water. The resulting xerogels were dried overnight in an oven at 100 °C.

It is important to state that silica xerogels were also obtained, but these results were not considered here because the preparations of these materials were time consuming and difficult to homogenize when compared to those xerogels obtained with TOPZ. Also, it was found that zirconium xerogels produce hard

pellets and a more reproducible signal when they interact with the laser beam.

Analytical signal calibration curves

Generally, LA-ICPMS requires a rather complex calibration procedure. The main reasons are the inconsistent relationship between the signal response in the ICPMS and the concentration of the analytes in the sample due to non-stoichiometric sampling during the ablation process and the incomplete vaporization and ionization of large particles in the plasma. Generally, the use of an internal standard (IS) technique is recommended.

The internal standards compensate for different ablation yields from both the sample and the standard and enable the preparation of a calibration curve. IS also compensates for the shot-to-shot variation and therefore improves the precision of the measurement. Fig. 2 presents the analytical signal of S, Ni, V and In. The raw signal (Fig. 2A) and the processed signal using the Savitzky–Golay smoothing filter (Fig. 2B) are presented. The signals were integrated between the dotted lines. Very stable signals were obtained after the signal processing so differences attributed to the laser integrations were satisfactorily compensated and this fact allows the construction of the calibration curves using the internal standard technique. No carbon depositions in the cones or splashing of the sample were observed during the analysis.

Table 2 presents the determination coefficient (R^2) of the calibration curves for Ni, S and V under the conditions given in the Experimental section. The models were fitted by a computer program Microsoft Excel which also tests the linearity by the F -test and automatically selects the linear calibration model. All calibration plots were linear over the whole used concentration range. A xerogel pellet without any standard addition as blank was used. R^2 values exceeded 0.990 with the exception of S and

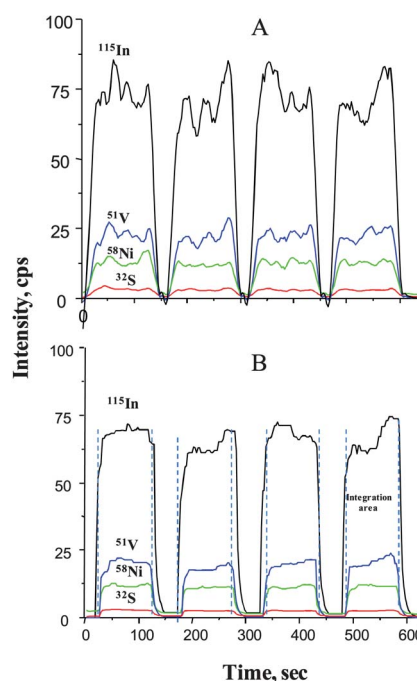


Fig. 2 Analytical signal: raw signal (A) and processed signal (B).

Table 2 Analytical figures of merit obtained for xerogel LA-ICP SFMS

Element	R^2			Sensitivity/ 10^4 , counts/ng g^{-1}			DL/ng g^{-1}			RSD (%)		
	TS	SG	OS	TS	SG	OS	TS	SG	OS	TS	SG	OS
Ni	0.9935	0.999	1.000	7.9	2.3	0.41	0.7	18	4.9	2.6	9.7	3.6
V	0.9983	0.999	0.999	4.7	3.9	1.66	0.8	23	3.5	2.9	3.4	1.9
S	0.9350	—	—	1.11	—	—	1.5	—	—	1.2	—	—

Table 3 Analysis of the crude oil samples using the xerogel method

Crude oil	Nickel/ $\mu g g^{-1}$			Vanadium/ $\mu g g^{-1}$			Sulfur (w/w%)		
	This study	Reference ^a	t_{exp}	This study	Reference ^a	t_{exp}	This study	Reference ^b	t_{exp}
Cerro Negro	125 \pm 11	143 \pm 10	2.37	492 \pm 36	534 \pm 54	1.20	2.8 \pm 0.1	2.9 \pm 0.7	0.25
South Europe	10.4 \pm 0.2	11.0 \pm 0.4	2.42	13.0 \pm 0.3	13.6 \pm 0.3	2.41	3.96 \pm 0.08	—	—
Africa	11.7 \pm 0.4	12.1 \pm 0.1	2.13	9.7 \pm 0.3	10.0 \pm 0.1	2.05	20 \pm 2 ^a	—	—
SYV	9.2 \pm 0.6	—	—	46 \pm 1	—	—	0.62 \pm 0.05	—	—

^a Direct introduction of the organic solution.²¹ ^b Digestion method,²² $t_{(0.05;6)} = 2.45$.

these values are slightly lower than those obtained in the analysis of crude oils with silica gel plate¹³ and direct introduction of organic solution methods²¹ using ICP-SFMS (values also presented in Table 2).

Sensitivity, detection limit, short term precision and long term stability

In this section, typical figures of merits: sensitivity, detection limit and short-term precision were used to evaluate the analytical performance of the xerogel pellets. Determination of limit of detection (LOD) was performed as the concentration of analyte, which produces a signal equal three times the standard deviation of the background fluctuations. Short-term precision was expressed as relative standard deviation (RSD) of the fluctuations in the emission signal around a mean value from a series of 10 replicates. Table 2 presents sensitivities, detection limits, and short-term precision for Ni, V and S. These figures of merits were compared to those obtained in the analysis of crude oils with silica gel plate and direct introduction of organic solution methods using ICP-SFMS. Limit of detections achieved for Ni and V using the xerogel are better than those obtained by the other studies thanks to the better sensitivities. Short-term precision values for S, Ni, and V are better than silica gel plates and direct injection of organic solutions. Unfortunately, it was not possible to contrast S values.

Crude oil analysis

Table 3 presents the results of S, Ni and V for the crude oil samples studied. Four crude oil samples having different API gravities were analyzed. Ni and V results were compared with the direct introduction of organic solutions with external calibration in ICP-SFMS.²¹ Statistical t -test showed that there were no significant differences between both methods. Similar result was

obtained with S in Cerro Negro crude oil. This value was compared to that obtained using the traditional digestion method.²²

Conclusions

The possibility of employing xerogel matrix for the analysis of crude oil samples by LA ICP-SFMS was successfully showed in this work. Zr n -propoxide is the recommended dispersion medium. Calibration curves made with encapsulated aqueous inorganic solutions using In as the internal standard are a good alternative for the LA quantitative analysis. The method provides analytical figures of merits that are similar to LA ICP SFMS studies with crude oils. Highly homogeneous distribution of the internal standard in the pellet leads to an improvement in accuracy and precision of the analytical results due to a better compensation for both the signal fluctuations and variations in the ablation process. Additional advantage of the xerogel method lies in the preparation of stable crude oil and aqueous standard targets.

Acknowledgements

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References

- 1 A. Montaser, M. G. Minnich, J. A. McLean and H. Liu, *Sample Introduction in ICP-MS in Analytical Atomic Spectrometry*, ed. A. Montaser, Wiley-VCH, New York, 1998.
- 2 R. Hutton, *J. Anal. At. Spectrom.*, 1986, **4**, 259.
- 3 D. Hausler and R. Carlson, *Spectrochim. Acta Rev.*, 1991, **14**, 125.

-
- 4 C. Duyck, N. Miekeley, C. L. Porto da Silveira, R. Q. Aucélio, R. C. Campos, P. Griberg and G. P. Brandão, *Spectrochim. Acta*, 2007, **62**, 939.
 - 5 J. S. F. Pereira, D. P. Moraes, F. G. Antes, L. O. Diehl, M. F. P. Santos, R. C. L. Guimaraes, T. C. O. Fonseca, V. L. Dressler and E. M. M. Flores, *Microchem. J.*, 2010, **96**, 4.
 - 6 K. Kahen, A. Strubinger, J. R. Chirinos and A. Montaser, *Spectrochim. Acta, Part B*, 2003, **58**, 397.
 - 7 P. Giusti, Y. Nuevo Ordonem, C. P. Lienemann, D. Schaumlöffel, B. Bouyssiere and R. K. Lobinski, *J. Anal. At. Spectrom.*, 2007, **22**, 88.
 - 8 C. Lord, *Anal. Chem.*, 1991, **63**, 1594.
 - 9 M. Murillo and J. Chirinos, *J. Anal. At. Spectrom.*, 1994, **9**, 247.
 - 10 M. A. Gondal, T. Hussain, Z. H. Yamani and M. A. Baig, *Talanta*, 2006, **69**, 1072.
 - 11 N. H. Bings, *J. Anal. At. Spectrom.*, 2002, **17**, 759.
 - 12 J. Heilmann, S. F. Boulyga and K. G. Heumann, *J. Anal. At. Spectrom.*, 2009, **24**, 385.
 - 13 N. Vorapalawut, P. Pohl, B. Bouyssiere and R. Lobinski, *J. Anal. At. Spectrom.*, 2011, **26**, 618.
 - 14 E. Ricard, C. Pécheyran, G. Sanabria, A. Prinzhofer and O. F. Donaid, *Anal. Bioanal. Chem.*, 2011, **399**, 2153.
 - 15 H. Podbielska, A. Ulatowska-Jarza, G. Müller and H. Eichler, *Sol-Gels for Optical Sensor in Optical Chemical Sensor*, ed. F. Baldini, A. Chester, J. Homola and S. Martellucci, Springer, Netherlands, 2006.
 - 16 H. Sela, Z. Karpas, H. Cohen, Y. Zakon and Y. Zeiri, *Int. J. Mass Spectrom.*, 2011, **307**, 142.
 - 17 M. Viger, J.-F. Gravel, D. Brouard, D. Beauchemin and D. Boudreau, *Anal. Chem.*, 2005, **77**, 706.
 - 18 J. Fitzpatrick, T. K. Kyser, D. Chipley and D. Beauchemin, *J. Anal. At. Spectrom.*, 2008, **23**, 244.
 - 19 I. Hubová, M. Holá, J. Pinkas and V. Kanicky, *J. Anal. At. Spectrom.*, 2007, **22**, 1238.
 - 20 D. Brouard, J. F. Gravel, M. L. Viger and D. Boudreau, *Spectrochim. Acta, Part B*, 2007, **62**, 1361.
 - 21 P. Pohl, N. Vorapalawut, B. Bouyssiere, H. Carrier and R. Lobinsky, *J. Anal. At. Spectrom.*, 2010, **25**, 704.
 - 22 F. Marciano, R. Flores, J. Chirinos and M. A. Ranaudo, *Energy Fuels*, 2011, **25**, 2137.