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Talanta 68 (2006) 957–962

Talanta

www.elsevier.com/locate/talanta

The development of a method for the determination of trace elements in fuel alcohol by ETV-ICP-MS using isotope dilution calibration

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Received 12 April 2005; received in revised form 22 June 2005; accepted 22 June 2005
Available online 1 August 2005

Abstract

A method for the determination of Ag, Cd, Cu, Pb and Tl in fuel alcohol by isotope dilution electrothermal vaporization inductively coupled plasma mass spectrometry (ID ETV-ICP-MS) is proposed. The analytes were separated in two groups: Ag and Cu were determined without modifier and Cd, Pb and Tl with the use of Pd as chemical modifier. The employed ETV operational conditions were pyrolysis temperature of 800 °C for Cd, Pb and Tl and of 900 °C for Ag and Cu and vaporization temperature of 2400 °C for both groups. Seven common, one with additive and one anhydrous fuel ethanol samples were analyzed. The spiked and reference isotopes were, respectively, ^{109}Ag and ^{107}Ag, ^{112}Cd and ^{111}Cd, ^{63}Cu and ^{65}Cu, ^{206}Pb and ^{208}Pb and ^{203}Tl and ^{205}Tl. The added amounts of the enriched isotope material were the same for all samples: 4.6 ng of ^{109}Ag, 5 ng of ^{112}Cd, 21.1 ng of ^{63}Cu, 9 ng of ^{206}Pb and 0.21 ng of ^{203}Tl. The blank was bi-distilled ethanol, acidified with 0.3% (v/v) nitric acid, as the samples. The limits of detection (LODs) were calculated as three times the standard deviation of the concentrations in the blank ($n = 10$) and were, in μg L^{-1}, for Ag: 0.02, for Cd: 0.08, for Cu: 0.1, for Pb: 0.05 and for Tl: 0.001. The obtained concentrations in the samples were in agreement with those obtained by external calibration (EC), according to the paired *t*-test. The isotope dilution (ID) showed to be a robust, fast and simple calibration technique for the analysis of fuel ethanol.

Keywords: Isotope dilution; Fuel ethanol; ETV-ICP-MS; Modifier; Trace elements

1. Introduction

The determination of metals in fuels is especially difficult due to their low concentrations and the lack of certified reference samples. The analysis of fuels is important, since the presence of some elements, such as Al, Ag, Cu, Fe and Ni, even in low concentrations, can promote the degradation and, consequently, a detriment in the performance of the fuel, corrosion and also the formation of deposits on motor parts [1]. In addition, toxic elements, such as As, Cd, Hg, Pb and Tl, can be released to the atmosphere by the combustion of fuels, representing an expressive source of pollution [2]. In Brazil, large amounts of fuel ethanol are used directly as automobile fuel or as oxygenated additive for the gasoline [3]. In this sense, the Cu concentration in the ethanol that is added to the gasoline has to be controlled, since this element promotes a partial decomposition of the gasoline. The concentrations of inorganic components in fuel ethanol are very low, since it is a distilled product. For this reason, very sensitive techniques of analysis are required. In addition, the lack of certified fuel samples makes necessary the use of artifices to demonstrate the accuracy of the methods, such as recovery tests or comparison between results obtained by different techniques or methods.

The inductively coupled plasma mass spectrometry (ICP-MS) is a well-established multielemental and sensitive technique of analysis. Besides the many advantages of this technique, the interferences can be its biggest disadvantage, although many of them are very well studied and can be corrected by calibration techniques or equations [4–6]. The coupling of an electrothermal vaporizer (ETV) to the ICP-MS confers to this technique, additional advantages. The sample injected inside the graphite tube of the ETV

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doi:10.1016/j.talanta.2005.06.047

is submitted to a temperature program, during which, the elimination of water and acids, as well as volatile components of the sample matrix, is desirable. By this procedure, the analytes can be conduced to the plasma during the vaporization step, free from most concomitants [7–9]. In addition, this coupling allows the analysis of many kind of samples that cannot be analyzed directly by ICP-MS using pneumatic nebulization, such as organic samples or samples containing high quantity of dissolved solids. The coupling ETV-ICP-MS has been successfully employed in our lab for the analysis of coal [10,11] and sediments as slurries [12–14] and gasoline as emulsion [15,16].

In this context, the ETV-ICP-MS allied to isotope dilution (ID) calibration has shown to be an adequate technique for the analysis of solid samples [17–19], slurries [11,12,20–22] and fuels [16]. The isotope dilution can be a helpful tool, since it is an almost free from interference calibration technique, because the concentration of the analytes is quantified in the sample itself. Then, the problems related to the different behaviors of samples and calibration solutions are eliminated [12,23]. In this calibration technique, an enriched isotope of the analyte is added to the sample and the concentration is calculated by the measurement of the altered isotope ratio of two isotopes of the analyte. This is a fast, simple and accurate calibration technique, requiring only an enriched isotope material of the analyte and that the analyte has at least two free from spectral interference isotopes or that the spectral interferences can be corrected. [24].

More recently, important causes of uncertainty related to the ID have been highlighted, among them, especially the mass discrimination can be responsible for erroneous determinations. In this case, the uncertainty is due to different mass discrimination extension between the two measured isotopes of the analyte, and should be corrected by analyzing a standard or certified reference material with known composition of the same element. An approach to estimate the mass discrimination is to quantify the isotope ratio of a certified enriched isotope standard of a different element. By this procedure, the uncertainties are corrected in a m/z ratio different to that of the analyte, such as the use of ^{65}Cu/^{63}Cu for the determination of ^{68}Zn/^{64}Zn and vice versa [25], ^{30}Si/^{28}Si in the determination of ^{34}S/^{32}S [26] and ^{205}Tl/^{203}Tl in the determination of ^{206}Pb/^{208}Pb [27] or in the determination of ^{200}Hg/^{199}Hg [28]. When the sample is not originated from a radioactive region, the correction of mass discrimination can be adequately performed by measuring the correction factor (K) with the sample itself. In our lab, we have applied ID to determine Pb, among other elements, in certified samples, estimating the uncertainties by measuring the isotope ratios in the sample and very accurate results have been obtained [11,12,29]. This procedure for the uncertainties correction will be applied in this work.

Another important concept in ID is the needing of the equilibration between the added spike and the analyte in the sample. According to Clough et al. [28], the equilibration is easily obtained for liquid samples by simple agitation, but not for solid samples. A non-complete equilibration yields erroneous results. In the case of organic samples, the analyte should be extracted to the aqueous phase in order to avoid problems concerning the equilibration, since the enriched isotope standard materials are, usually, in the inorganic form. In previous works with fuels [15,16,30], we have added nitric acid to the samples to guarantee the complete analyte conversion into the inorganic form. In addition, it also can be that the equilibration between the analyte and the spike occurs in the ETV cell during the application of the temperature program. This hypothesis is reinforced by accurate results obtained in the analysis of slurries by ID ETV-ICP-MS [11,12,20–22,31].

Concerning the analysis of fuel, the ID was employed by Evans et al. [26] to determine sulfur in diesel fuel by high resolution ICP-MS. We were the first to employ the ID ETV-ICP-MS to the analysis of gasoline prepared as oil-in-water emulsions [16], but no report has been found applying this technique to the direct analysis of alcoholic samples.

The goal of this work is to use the ID ETV-ICP-MS to develop a method for the determination of Ag, Cd, Cu, Pb and Tl in fuel ethanol. The resulting concentration values will be compared to the results obtained by external calibration in another work [32]. By this procedure, we intend to avoid the use of recovery tests to guarantee the accuracy of the method.

2. Experimental

2.1. Instrumentation

An ELAN 6000 inductively coupled plasma mass spectrometer, from Perkin-Elmer Sciex (Thornhill, Toronto, Canada), coupled to a HGA 600 MS electrothermal vaporizer and an AS-60 auto-sampler (both from Perkin-Elmer) was used. The same instrumental parameters used in another work [32] were applied.

The spiked and reference isotopes were, respectively, ^{109}Ag and ^{107}Ag, ^{112}Cd and ^{111}Cd, ^{63}Cu and ^{65}Cu, ^{206}Pb and ^{208}Pb and ^{203}Tl and ^{205}Tl.

2.2. Reagents

The reagents used in this work were all of analytical grade, unless otherwise specified. The water (resistivity of 18.2 MΩ cm) was de-ionized in a Milli-Q system (Millipore, Bedford, MA, USA). Nitric acid and ethanol (both from Carlo Erba, Milan, Italy) were further purified by sub-boiling distillation in a quartz still (Kürner Analysentechnik, Rosenheim, Germany). The following enriched isotope standard materials were employed: ^{109}Ag (99.2%, as metal), ^{112}Cd (97.55%, as oxide), ^{63}Cu (99.89%, as metal), ^{206}Pb (99.8%, as carbonate) and ^{203}Tl (96.27%, as oxide) from Cambridge Isotope Laboratories, INC. (Andover, MA, USA), prepared by dissolution in 2% (v/v) HNO_3.

The software of the spectrometer calculates the analytes concentrations after measuring the altered isotope ratios. The ratio of the signal intensities of the isotopes in the samples, without the addition of the enriched isotope, was compared to the natural ratio to check for spectral interference and to correct for mass bias. This correction procedure is carried out for each sample before the measurement of the respective sample enriched with the spike, resulting in a correction factor for each sample, which includes the correction of instrumental mass discrimination and variations in the natural isotope abundance ratio. It was observed that the correction factor did not vary significantly for the different samples, even for Pb. It can be expected that, in a routine analysis with a large number of samples, an average value for the correction factor for each analyte can be satisfactorily employed, in order to reduce the total analysis time, since the samples have similar matrices.

A 0.1% (w/v) Pd solution prepared from a palladium modifier solution, 10.0 g L^{-1} Pd as Pd nitrate (No. 1.07289.0050 from Merck, Darmstadt, Germany) was employed as modifier. When the modifier was added, a 10 μL of the 0.1% (w/v) Pd solution was pipetted into the graphite tube together with 20 μL of the sample or of the calibration solution, resulting in an injection of 10 μg of Pd into the tube.

2.3. Samples

Nine fuel ethanol samples were analyzed, i.e., eight hydrated fuel ethanol samples (AEHC, from the Portuguese: *álcool etílico hidratado combustível*) bought in different local gas stations and one anhydrous fuel ethanol sample (AEAC, from the Portuguese: *álcool etílico anidro combustível*), supplied by Petrobrás (Rio de Janeiro, RJ, Brazil). Among the AEHC samples, seven were of common fuel ethanol (C1–C7) and one of them was an additive added fuel ethanol (A1), what means that detergents were added to the fuel, with the objective of cleaning the motor parts.

The samples were prepared by addition of the adequate amounts of the enriched isotope material and then acidified by the addition of 0.3% (v/v) nitric acid. The added amounts of the enriched isotope material were the same for all samples: 4.6 ng of ^{109}Ag, 5 ng of ^{112}Cd, 21.1 ng of ^{63}Cu, 9 ng of ^{206}Pb and 0.21 ng of ^{203}Tl.

The blank was bi-distilled ethanol, acidified with 0.3% (v/v) nitric acid, as the samples.

3. Results and discussion

3.1. Optimizations

The ETV temperature program was optimized previously [32], for aqueous and ethanolic solutions. For the more volatile elements, Pd in solution was used as chemical modifier and, for the less volatile analytes, no modifier was employed. It was observed that the Pd modifier interfered on the determination of Ag. Their mass/charge ratios are not exactly coincident, Ag has two isotopes, ^{107}Ag and ^{109}Ag, and Pd has six, among them ^{106}Pd, ^{108}Pd and ^{110}Pd, but since the modifier is added in large excess, a partial superposition in the mass spectrum is expected to occur. Without modifier, the Ag thermal stability was kept up to about 1000 °C pyrolysis temperature. For this reason, the determination of Ag in fuel ethanol by ID ETV-ICP-MS was carried out without modifier.

Substantial interferences were not observed over the other analytes isotopes in fuel ethanol samples. Besides the Pd interference over Ag, only ZrO or YO can interfere over Ag isotopes, but these elements are not commonly present in these samples. The reference ^{111}Cd isotope is interfered only by MoO, but the oxides were limited in less than 3% through the Daily Performance optimization. In the case of the ^{112}Cd enriched isotope, interference by ^{112}Sn was mathematically corrected by the software. No spectral interference is reported over Pb and the interferences over Cu or Tl isotopes are only due to oxides or Ba^{2+} that were limited, as checked by the Daily Performance. Non-spectral interferences do not occur in isotope dilution calibration, since the calibration is carried out with the sample itself and mass bias were corrected by measuring the correction factor (K) also with the sample.

The sensitivity of the ICP-MS technique decreases by the transient nature of the generated signals, limiting the number of detectable analytes by this approach. In addition, the concentrations of these analytes in these samples are very low. Since in ID, two isotopes of each analyte have to be measured, the employment of ID with the ETV additionally limits the number of analytes. For this reason, the analytes were separated in two groups: the more volatile analytes that require the use of a modifier, Cd, Pb and Tl, were determined with Pd in aqueous solution as chemical modifier; and the less volatile analytes, Ag and Cu, that do not need the modifier. The pyrolysis temperatures for the determination of the analytes in the fuel ethanol samples were, respectively, 800 °C for Cd, Pb and Tl and 900 °C for Ag and Cu.

The vaporization temperature and inner gas flow rate were optimized previously [32]. In this work, a 2400 °C vaporization temperature and a 300 mL min^{-1} inner gas flow rate were employed for all analytes.

3.2. Limits of detection and precision

The limit of detection (LOD) was defined as three times the standard deviation of the obtained concentrations in the blank, using ten replicates. For the measurement of the analytes concentrations in the blank, the same amounts of the enriched isotope standards added to the samples were added to the blank. The software of the equipment calculates the analyte concentration in the blank by the alterations in the isotope ratios produced by the addition of the enriched isotope standard. The obtained LODs were, in μg L^{-1}: 0.02 for Ag, 0.08 for Cd, 0.1 for Cu, 0.05 for Pb and 0.001 for Tl.

The precision of the method was evaluated by the relative standard deviation (R.S.D.) of five measurements of the sam-

Table 1
Figures of merit for the determinations by external calibration (EC) [32] and by isotope dilution (ID)

Analyte	EC		ID	
	LOD (μg L^{-1})	R.S.D. (%)	LOD (μg L^{-1})	R.S.D. (%)
Ag[a]	0.02	9.1	0.02	5.8
Cd[b]	0.07	25.4	0.08	3.7
Cu[a]	0.2	6.6	0.1	3.4
Pb[b]	0.02	3.1	0.05	1.8
Tl[b]	0.0008	2.5	0.001	11.2

R.S.D. ($n = 5$) for the C7 sample.

[a] Without modifier.

[b] With 10 μg of Pd.

Table 2
Concentrations, in μg L^{-1}, of the more volatile elements in the fuel ethanol samples, measured by external calibration (EC) [32] and by isotope dilution (ID)

Sample	Cd		Pb		Tl	
	EC	ID	EC	ID	EC	ID
C1	0.36 ± 0.11	0.41 ± 0.02	0.51 ± 0.17	0.62 ± 0.02	0.0021 ± 0.0011	<LOD
C2	0.54 ± 0.17	0.53 ± 0.08	0.93 ± 0.10	0.98 ± 0.07	0.0026 ± 0.0013	0.0013 ± 0.0007
C3	0.08 ± 0.05	0.06 ± 0.02	0.60 ± 0.02	0.60 ± 0.05	0.0029 ± 0.0016	0.0025 ± 0.0007
C4	0.07 ± 0.05	0.08 ± 0.05	0.39 ± 0.02	0.41 ± 0.07	0.0030 ± 0.0009	0.0028 ± 0.0010
C5	<LOD	0.02 ± 0.02	0.92 ± 0.07	1.09 ± 0.10	0.0045 ± 0.0010	0.0041 ± 0.0010
C6	0.09 ± 0.02	0.07 ± 0.05	1.51 ± 0.27	1.58 ± 0.02	0.0042 ± 0.0008	0.0047 ± 0.0005
C7	0.24 ± 0.11	0.20 ± 0.08	0.58 ± 0.05	0.51 ± 0.05	0.0039 ± 0.0016	0.0047 ± 0.0007
A1	0.09 ± 0.00	0.07 ± 0.05	0.52 ± 0.08	0.56 ± 0.14	0.0010 ± 0.0008	0.0021 ± 0.0012
AEAC	1.15 ± 0.30	1.32 ± 0.25	1.21 ± 0.12	1.17 ± 0.02	<LOD	<LOD

C1–C7: common hydrated fuel ethanol, A1: hydrated fuel ethanol with additive, AEAC: anhydrous fuel ethanol.

ple C7. The obtained R.S.D.s are in the Table 1, as well as the LODs for comparison with the values obtained by external calibration [32]. In general, the LOD values obtained by isotope dilution were in the same order of magnitude as the LODs obtained by external calibration, but better RSDs were obtained with ID, except for Tl.

3.3. Analytical performance

The obtained analytes concentrations employing the ID proposed method, as well as the obtained concentration values employing external calibration against ethanolic solutions, are presented in the Tables 2 and 3. The concentrations obtained for each analyte, by both methods, were in agreement according to the paired *t*-test for a 95% confidence level. This indicates the accuracy of the ID method, since the external calibration method [32] was validated by recovery tests.

The concentrations obtained by both methods are additionally showed in correlation graphs in the Fig. 1. It can be observed from these graphs that the correlation coefficients for the analytes were very close to 1, except for Tl, which value was 0.9364, although the results were in agreement when the paired *t*-test was applied. This is not a contradiction, since the high standard deviations obtained for this element that has very low concentrations in the analyzed samples, is used in the paired *t*-test calculation.

Table 3
Concentrations, in μg L^{-1}, of the less volatile elements in the fuel ethanol samples, measured by external calibration (EC) [32] and by isotope dilution (ID)

Sample	Ag		Cu	
	EC	ID	EC	ID
C1	0.059 ± 0.012	0.063 ± 0.010	11.25 ± 0.77	11.41 ± 0.43
C2	0.022 ± 0.008	0.014 ± 0.010	13.52 ± 1.14	14.67 ± 1.01
C3	0.044 ± 0.010	0.036 ± 0.011	3.64 ± 0.22	4.20 ± 0.45
C4	0.035 ± 0.010	0.037 ± 0.007	1.80 ± 0.32	1.96 ± 0.12
C5	0.065 ± 0.013	0.059 ± 0.010	4.46 ± 0.30	4.61 ± 0.35
C6	0.072 ± 0.017	0.079 ± 0.005	4.16 ± 1.02	4.27 ± 0.35
C7	<LOD	0.010 ± 0.005	2.49 ± 0.42	3.03 ± 0.45
A1	0.062 ± 0.010	0.068 ± 0.005	14.98 ± 0.82	14.44 ± 0.72
AEAC	0.038 ± 0.010	0.031 ± 0.005	3.72 ± 0.57	3.50 ± 0.37

C1–C7: common hydrated fuel ethanol, A1: hydrated fuel ethanol with additive, AEAC: anhydrous fuel ethanol.

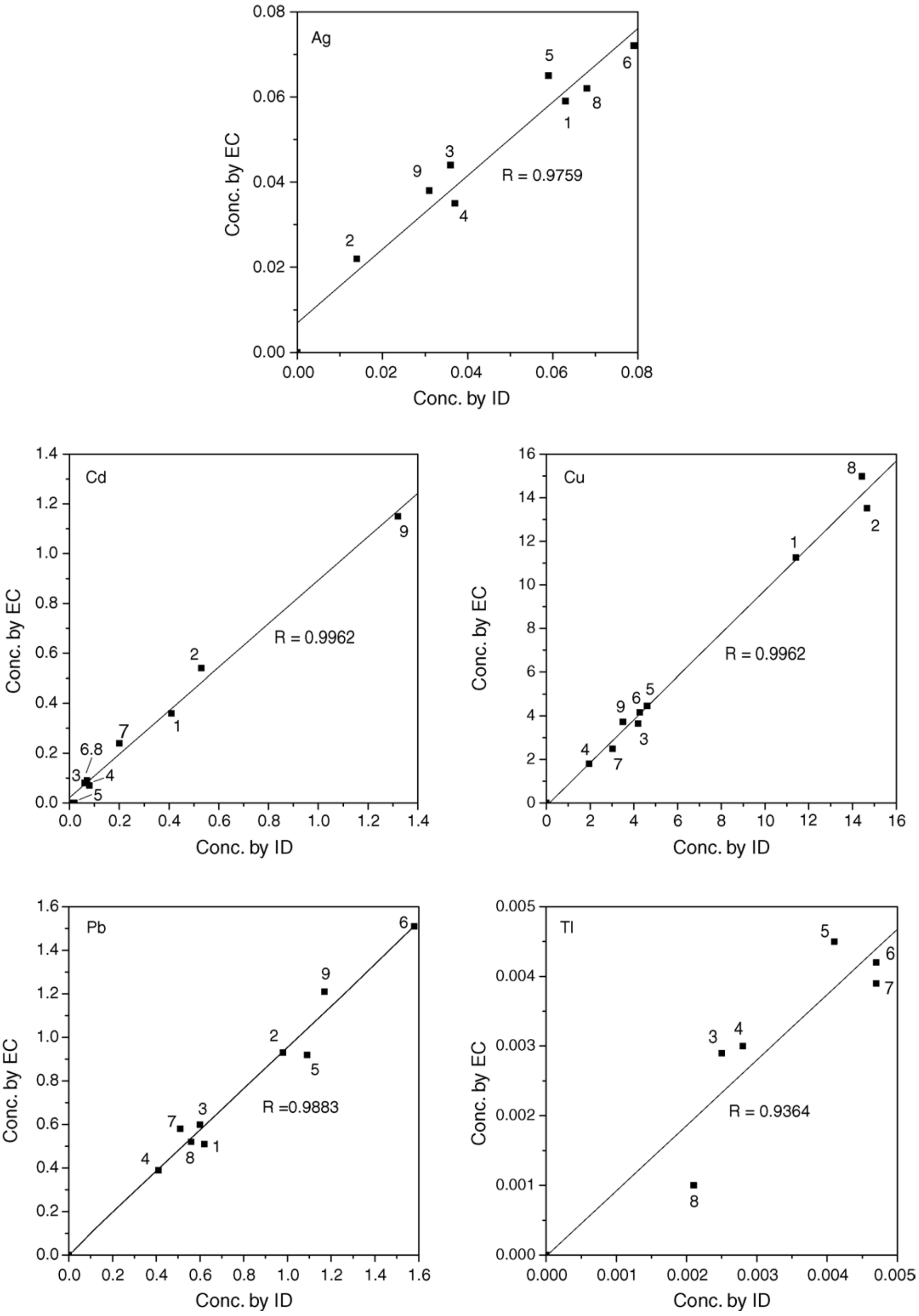

Fig. 1. Correlations graphs for the analytes concentrations in the fuel ethanol samples, in μg L^{-1}, measured by external calibration (EC) and isotope dilution (ID) ETV-ICP-MS. Samples C1–C7: 1–7; sample A1: 8 and sample AEAC: 9. R is the correlation coefficient.

4. Conclusion

At this time, one could ask: why to employ the isotope dilution to analyze fuel ethanol? Which are the advantages of the isotope dilution over the external calibration with ethanolic solutions? The answer may not be so obvious because isotope dilution is still not so usual and not so easy to understand in the first moment. But we can certainly say that this calibration technique makes the analysis very simple, fast and clean. The addition of the enriched isotope material is just one step of the sample preparation. There is no need of recalibration, and last, but not least, this compensates the most interference that occur in ICP-MS, generating results that were in agreement to those obtained by external calibration.

Acknowledgements

The authors thank Agência Nacional de Petróleo (ANP) and Conselho Nacional de Pesquisas e Desenvolvimento Tecnológico (CNPq, Project CTPETRO 501744/2003-7) for financial support. A.J. Curtius and T.D. Saint'Pierre have each a research scholarship from CNPq.

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