http://dx.doi.org/10.5935/0103-5053.20140079

J. Braz. Chem. Soc., Vol. 25, No. 6, 1062-1070, 2014.
Printed in Brazil - ©2014 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Article

Determination of Rare Earth Elements in Spent Catalyst Samples from Oil Refinery by Dynamic Reaction Cell Inductively Coupled Plasma Mass Spectrometry

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A determinação de elementos terras raras (REE) em catalisadores gastos provenientes da indústria de petróleo é proposta. Foram testados três procedimentos de tratamento de amostra, um sem adição de HF e outros dois usando diferentes quantidades de HF e ácido bórico, além de uma etapa de evaporação assistida por radiação micro-ondas para dissolução dos fluoretos de REE. O meio contendo 1,0 mL de HF e 8,0 mL de ácido bórico foi eficiente para promover a completa digestão da amostra. Estudos foram realizados usando uma célula de reação para redução de interferências por íons poliatômicos para quatro elementos por espectrometria de massas com plasma acoplado indutivamente (ICP-MS). Material de referência certificado, TDB-1, foi utilizado para avaliar a exatidão do método aplicado a dez amostras de catalisadores. O procedimento proposto é rápido, eficiente e apresentou exatidão e precisão adequadas para 14 dos 16 analitos determinados. Testes de adição e recuperação apresentaram valores entre 87% e 101%.

The determination of rare earth elements (REE) in spent catalyst samples from oil refinery is proposed. Three sample treatment procedures were tested, one without HF and two using different amounts of HF and boric acid. A microwave evaporation step to promote the dissolution of the REE fluorides was carried out. The medium containing 1.0 mL of HF and 8.0 mL of boric acid promoted the complete digestion. Studies were carried out using a reaction cell to overcome polyatomic interferences on four elements by inductively coupled plasma mass spectrometry (ICP-MS). Certified reference material, TDB-1, was used to evaluate the method accuracy applied to ten spent catalysts. The sample treatment is fast and promotes the complete digestion of the samples and the developed procedure led to proper accuracy for 14 of the 16 determined analytes. Recovery tests presented values between 87% and 101%.

Keywords: rare earth elements, FCC spent catalyst, sample preparation, DRC-ICP-MS

Introduction

The world demand for rare earth elements (REE) is heightening drastically as a consequence of the widespread use of high-tech products and since the renewable and environment friendly energy technologies, well promoted nowadays, are possible only because the occurrence of these elements. The REE demand will continue to grow as the life conditions in many countries, as for example China and India, are more and more improving.[1]

The REE, 15 from f-block, the lanthanides, and 2 others from d-block, scandium and yttrium, are not really rare, but because their similarities, their isolation and separation are difficult, and since their occurrence is highly dispersed, their production is expensive.[2] To supply the increasing demand and the deficit caused by China's export restrictions, many countries are developing REE mining and it is expected that in few years the world production will grow significantly. Even so, there is no guarantee that this increase in the production will be enough to supply the growing demand. Furthermore, the REE extraction from natural sources is becoming even more difficult, because the ores are becoming poorer, and mining activities are related to important environmental

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issues. This calls attention to another important governmental concern: reducing the environmental impacts caused by the use of modern technologies.[3]

The growing use of high-tech products has increased the production of solid wastes containing REE. To be in line with the new tendencies for environmental protection reduce, recover, reuse and recycle concept is being adopted all over the world.[4] In Brazil, the national policy for solid wastes establishes the proper management of solid waste and requires the industrial sector to implement the recycling of residues from their process.[5] A correct management implies in a full understanding of the nature and the contents of the wastes, which requests analytical investigations. But, these investigations can be difficult since solid wastes are, normally, highly complex matrix samples and their conversion in a proper medium, making it possible the determination of elements by suitable analytical techniques, is still a challenge.[6]

Oil refinery industry generates huge amounts of solid waste from the most widely process used in petroleum refining, the fluid catalytic cracking (FCC). In this process, catalysts containing high concentrations of REE are used to convert heavier oil into lighter and more valuable products.[7] However, gradually the catalyst loses its activity and is rejected as a solid waste. Each year, hundreds of thousands of tons of spent catalysts are produced and many applications and re-use, such as masonry block, road construction and cement mortars, are proposed. But, considering the crucial importance of REE, their indispensable role in technologies, the high economic and environmental costs associated with their production by mining activities, spent catalysts could have a better destination. The use of spent catalyst as a source of REE would be an interesting application, supplementing their production from virgin ores, and also be in agreement with the recycling-recovery concept. Hence, investigations are needed to evaluate the amount and which REE remained in spent catalysts after the cracking process.[8]

Many techniques to analyze samples containing REE have been reported, but inductively coupled plasma mass spectrometry (ICP-MS) is considered the most powerful technique for this purpose. The ICP-MS attractiveness is mainly due to its high sensitivity, multi-elemental capacity, isotopic measurements possibility and a large linear working range.[9] Nonetheless, the determination of REE, by ICP-MS, finds some drawbacks since they are refractory and the formation of oxides is not negligible. Lighter REE oxides and hydroxides can cause polyatomic interferences on heavier REE. Oxides and hydroxides of Ba can cause spectral overlap on middle REE and oxides or hydroxides of Te can interfere with the lighter REE.[10] To overcome this problem, many approaches have been proposed, including measurement of doubly charged ions, use of algebraic corrections, instrumental parameters modifications and the application of desolvation techniques. Lately, a solution proposed with a great potential to overcome polyatomic interferences is the use of a dynamic collision/reaction cell, into which a gas is introduced to eliminate or reduce the polyatomic ions. Some example of gases used are, ammonia, helium, hydrogen, methane, xenon and neon.[11]

The determination of the analytes with reproducible and accurate results, in routine analysis, has the complete digestion of the sample as prerequisite. The sample preparation has been considered the most important step before the determination by ICP-MS. Methods for sample treatment include alkali fusion, open and closed digestion on hot plate and microwave-assisted digestion. Despite being effective, alkali fusion presents some disadvantages, such as the use of large amounts of fluxing agent, possible contamination, high blank levels, time consumption and tedious. Digestion on hot plate is successfully applied to mafic rocks, a type of mineral with high content of iron and magnesium, but for refractory minerals it does not promote the complete dissolution of the sample. Microwave-assisted digestion is also reported not to be so effective in accomplishing the complete dissolution of the sample, especially geological samples. Nevertheless its use has being increased recently due to some attractiveness, such as, high temperature and pressure, sealed vessels that decrease losses, increased digestion efficiency and its safety for the analyst. Furthermore, its full potential is still being exploited as reported by Muratli *et al.*,[6] who proposed a procedure using microwave to evaporate the acids fumes drawing them out through a series of bubblers containing boric acid, NaOH, and water. Also, Navarro *et al.*[12] described a procedure in which, after the digestion steps, a microwave-assisted step was carried out to accomplish the complete drying of the samples and solubilize the fluorides.

ICP-MS instrument using a conventional nebulization system requires the samples to be completely solubilized since any particle could clog the nebulizer. Many types of wastes contain high contents of silica, demanding the use of hydrofluoric acid to accomplish the complete dissolution of the matrix. However, it is well known that REE form insoluble complexes with hydrofluoric acid, making it impossible the introduction in ICP-MS instrument. Furthermore, the use of hydrofluoric acid can damage the components of the sample introduction system, when working with conventional nebulization manufactured in glass or quartz. Methods using HF with or without its elimination have been proposed for different types of samples, but few accomplish the complete decomposition of the samples and are time consuming and laborious.[6,12]

The goal of this work is to develop a fast and reliable method for determination of REE concentration in spent catalyst samples using microwave-assisted digestion and evaporation procedures to promote the complete decomposition of the samples and the dissolution of the REE fluorides. After the digestion of the samples the measurements of the analytes were carried out by ICP-MS, using ammonia in a reaction cell to overcome polyatomic interferences on the signal of four elements. At the best of our knowledge, the procedure developed in this work is a novelty for this type of samples, whose REE content has a great economic and environmental appeal.

Experimental

Instrumentation

In this work, an inductively coupled plasma mass spectrometer, model NexION (Perkin Elmer, Shelton, CT, USA) equipped with a sample introduction system by a peristaltic pump, a cross flow nebulizer and a concentric chamber, was used in all studies for procedure development to determine the concentration of REE. The instrument is also equipped with a dynamic reaction/collision cell, into which a gas is introduced with the purpose to overcome REE polyatomic interferences. Argon gas, 99.996 purity, (White Martins, São Paulo, SP, Brazil) was used in all measurements on the ICP-MS. Ammonia (99.995 purity, White Martins) was used in the studies of the polyatomic interferences on the elements of interest. The operational parameters of the ICP-MS instrument are shown in Table 1.

The sample treatments were carried out in a microwave oven model Ethos Plus, (Milestone, Sorisole, Italy). The instrument has an evaporation accessory VAC 1000 (Milestone) coupled to the microwave oven to accomplish the dissolution of the insoluble fluorides. Microbalance (Mettler, Toledo, Switzerland) was used on the mass measurements for all samples.

Reagents, standards and samples

All reagents used in this work were at least of analytical grade purity. Water purified in a system, Milli-Q (Millipore, Bradford, MA, USA), to a resistivity of 18.2 MΩ cm was used in preparing all samples and solutions. Nitric acid 65% v/v (Carlo Erba Reagenti, Milan, Italy) and hydrochloric acid 37% v/v (Vetec Rio de Janeiro, Brazil), used in all solutions, were purified by double sub-boiling distillation in a quartz still (Kürner Analysentechnik, Rosenheim, Germany). Hydrofluoric acid was also purified by double sub-boiling distillation in a poly(tetrafluoroethylene) system (Kürner Analysentechnik). To accomplish the dissolution of the insoluble fluorides boric acid (Vetec, Rio de Janeiro, RJ, Brazil) in a concentration of 5.0% m/v, was used in the microwave-assisted evaporation step after the digestion procedure. Multi-elemental solution of REE (Perkin Elmer, Shelton, USA) was used in the studies and calibration curves, 5.0 to 120 µg L^{-1}, for the analytes determination.

Table 1. Operational conditions of the ICP-MS instrument for REE determination in certified material, TDB-1, and in spent catalyst samples

RF power	1600 W
Detector voltage	
Pulse	1250 V
Analogical	–1675 V
Gas flow rate	
Principal	18 L min^{-1}
Auxiliary	1.2 L min^{-1}
Nebulizer	1.02 L min^{-1}
Sampler and skimmer cones	Ni
Signal measurements	Peak hopping
Reading per replicate	50
Auto lens mode	On
Dead time	35 ns
Detector operation mode	Pulse
Dwell time	25 ms
Corrections equations	–0.012780 I(^{157}Gd) for Sm –0.047902 I(^{166}Er) for Dy
Rejection parameter q of DRC mode	0.45

Ten samples of FCC spent catalysts from oil refining industry in different regions of Brazil was used to carry out the studies of sample treatment and the polyatomic interferences, as well as the determination of the concentration of REE. In absence of certified catalyst sample, a reference material with high content of silica, a rock sample, TDB-1, (CCRMP, Ottawa, Canada) was submitted to all procedures to evaluate the efficiency of the sample treatment and the accuracy.

Procedures

In a first sample treatment carried out, 100.0 mg of the FCC spent catalyst was weighed directly into the Teflon vessel, 4.0 mL of nitric acid, 2.0 mL of hydrochloric acid and 2.0 mL of hydrogen peroxide was added and the mixture was kept standing for 1 h to avoid strong reactions inside the instrument. Hydrogen peroxide was added because the samples were used in oil refining process, containing organic compounds and the coke formation within the porous is promoted. After this time, the samples were submitted to the microwave program. The temperature program for the digestion procedure assisted by microwave is shown in Table 2. After that, the solutions were transferred to 50.0 mL polyethylene tubes and diluted to a final volume of 50 mL with deionized water. In order to evaluate the accuracy of the method, a certified material, rock sample TDB-1, was also submitted to the same procedures.

Table 2. Temperature program for microwave digestion procedure of spent catalyst samples with and without HF for REE determination by ICP-MS

time / min	Step
5	Heating, from 20 °C to 140 °C
5	Heating, from 140 °C to 210 °C
15	Plateau, 210 °C
15	Ventilation, cooling down to 20 °C

A second treatment aiming to accomplish the total digestion of the samples was carried out. About 100.0 mg of one catalyst sample or reference material, TDB-1, was weighed directly into the Teflon vessels, 4.0 mL of nitric acid, 1.0 mL of hydrochloric acid and 1.0 mL of hydrogen peroxide were added and the mixture was kept standing for 1 h. Two procedures using HF were then adopted. In the first, 0.5 mL of HF was added and in the second, 1.0 mL of HF was added. The vessels were closed and submitted to the same microwave assisted program presented in Table 2. After the digestion and cooling steps, the vessels were opened and the covers were rinsed with 10 mL of high purity water into the digestion flasks. Then, when 0.5 mL of HF was used in the digestion procedure, 4.0 mL of boric acid saturated solution (5.0% m/v) was added and when 1.0 mL of HF was used, the volume of boric acid saturated was 8.0 mL. The vessels were covered with proper evaporation adapters and submitted to an evaporation microwave assisted program. In this evaporation program, the power was controlled instead of the temperature. The microwave program, suitable for the elimination of 15 mL of the acid solution, is presented in Table 3. After the evaporation step and cooling, the samples were transferred to 50.0 mL polyethylene tubes and filled up to a final volume of 50 mL with deionized water.

Table 3. Microwave program for 15 mL of acid solution evaporation, using boric acid to accomplish the dissolution of REE fluorides, for determination by ICP-MS

time / min	Power / W
6	250
6	450
6	650
6	250

Results and Discussions

Sample treatment

The first sample treatment was carried out using nitric and hydrochloric acids and oxygen peroxide to evaluate whether this medium would promote the complete sample digestion or the extraction of the analytes and, in this case, in an effective degree. H_2O_2 was used because it improves the decomposition of organic matter. This treatment did not promote the complete dissolution of the samples and solid particles remained after digestion process. Measurements by ICP-MS were carried out using the supernatant to quantify the concentration of the analytes and to evaluate the degree of extraction. For the certified material, TDB-1, the results presented in Table 5 (values obtained without HF) were in agreement for nine of the sixteen elements whose concentrations were determined. For others seven elements, the results were not in accordance.

In order to improve the efficiency of the digestion procedure, to obtain the complete decomposition of the samples and, consequently, to achieve the determination of the total amount of the analytes, a second treatment procedure using hydrofluoric and boric acids, with an evaporation step after the digestion, was carried out. For this treatment, 100.0 mg of the certified material were used and the digestion and evaporation steps were carried out as described in the procedures. The procedure carried out using 0.5 mL of HF in the digestion step and 4.0 mL of boric acid, in the evaporation step, was not efficient in promoting the complete dissolution of the samples. At the end of the procedure there still remained a small amount of solid particles. After applying the procedure with 1.0 mL of HF and 8.0 mL of boric acid, the obtained solutions were limpid and completely free of precipitate, showing the efficiency of both, the digestion of the silica and the dissolution of the REE fluorides. After that, the concentration of the analytes was determined by ICP-MS using the optimized parameters of the instrument, nebulizer gas flow rate and RF power, to promote the minimum oxide formation and also correction equations, according to the optimized parameters presented in Table 1. For twelve elements, the concentration values, calculated as mean ± 95% confidence interval (n = 3) according to student-*t* test, in the certified material were in agreement with the provided values and only four elements, Gd, Lu, Nd and Yb, the obtained values were discordant with the provided values for the certified material.

Polyatomic interferences

Since the complete dissolution of the sample was achieved and for four elements the obtained concentration values were discordant, meaning above or below the values for certified material, a study was performed to verify whether the presence of polyatomic ions would be interfering on the signal of the analytes and affecting the results. The isotope ^{158}Gd can suffer interference of the ions ^{141}Pr^{16}O^{1}H, ^{142}Nd^{16}O, and ^{142}Ce^{16}O. The signal of ^{175}Lu is affected by ^{158}Gd^{16}O^{1}H and ^{159}Tb^{16}O. The ion ^{126}Te^{16}O interferes with ^{142}Nd and ^{158}Gd^{16}O with ^{174}Yb.

To carry out this study, the certified sample submitted to the digestion and evaporation procedures, with the addition of REE solution equivalent to 10.0 µg L^{-1}, was used to evaluate whether ammonia would be effective in overcoming the interferences and its optimum flow rate. Figure 1 presents the effect of ammonia on the background equivalent concentrations for Gd, Lu, Nd and Yb. The effect of ammonia on the interferences was evaluated considering the background equivalent concentration (red line), calculated as the ratio between the analyte signal in the sample solution (blue line) and in the blank solution (green line). The results show that, for all analytes, there is a reduction in the background equivalent concentration as the ammonia flow rate increases. For Gd and Nd, this decrease is all over the flow rate range studied. For Lu, at first, an increase in the background equivalent concentration is observed up to 0.4 mL min^{-1} flow rate, then it decreases. The behavior of Yb is quite different. A small decrease is observed in the background equivalent concentration up to a rate of 0.4 mL min^{-1}. After that, an increase in the background equivalent concentration occurs probably because ammonia promotes the formation of polyatomic interfering ions with other elements present in the blank solution.

From Figure 1 it is also possible to see that the decrease in the background equivalent concentration is also because an increasing in the analytes signal with the increase of the ammonia flow rate. This is consistent because REE are refractory and tend to form oxides so, as the ammonia flow rate increases, possibly the oxide bonds are broken resulting in a growing of the analyte signal. However, at higher gas flow rate the analyte signal decreases, probably because ammonia in excess behaves as collision gas and the analyte is withdrawn out of the cell by collision. This decrease is not so significant, except for Gd. The ammonia flow rate that promotes the best background equivalent concentration for each analyte was chosen as the best combination between the analyte signal (blue line) and the blank solution signal (green line). The ammonia flow rate was 0.4 mL min^{-1} for Yb and 0.7 mL min^{-1} for Gd, Lu and Nd, respectively.

Sample dilution

The concentration of REE varies greatly in the sample. In this case, the sample dilution is an important factor in performing the determination of all analytes

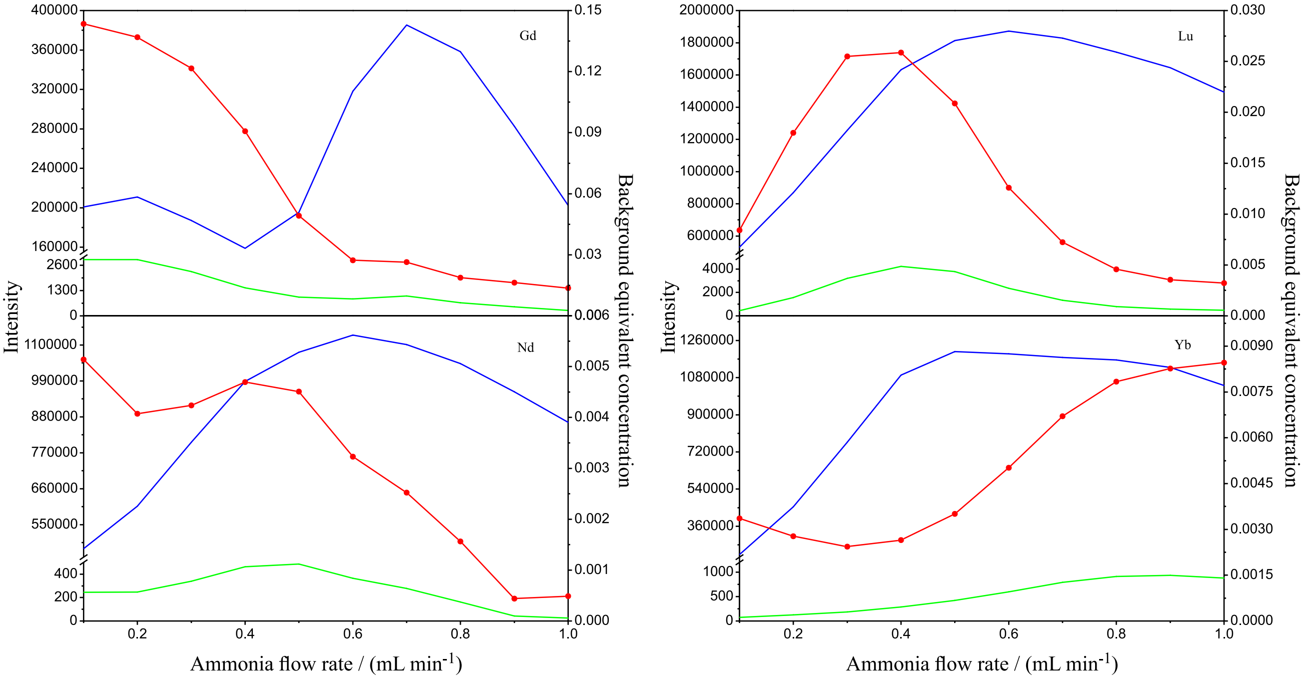

Figure 1. Effect of ammonia gas on the background equivalent concentration (-•-) of REE for the certified material TDB-1, with the addition of 10.0 µg L^{-1} of the analytes.

simultaneously. Besides, a proper dilution of the solutions introduced into ICP-MS instrument is required because high concentration of acids can damage the components, as for instance the cones. Normally solutions with an acid concentration of 1.0% are used. However, the sample treatment developed in this work, which included an evaporation step, accomplished the elimination of great part of the acids, not being necessary such high dilution. Thus, solutions were prepared by diluting the sample 10, 20 and 50 folds, considering the variation of the analytes concentration, and HNO_3 was added to assure a 1.0% acid concentration. The dilution, in which all analytes were simultaneously determined leading to values in agreement with the certified material for all elements, was 20 times. So, for the determination of REE elements in the spent catalyst samples a 20 times dilution was adopted.

Sample determination

After the studies for the sample treatment and the polyatomic interferences corrections by ICP-MS with a reaction cell, a procedure for determination of 16 REE in the certified material, TDB-1, was proposed. In this method, 12 elements, Ce, Dy, Er, Eu, Ho, La, Pr, Sc, Sm, Tb, Tm and Y, would be measured in the standard mode of the instrument. On the other hand, the determination of Gd, Lu, Nd and Yb would be carried out using ammonia as reaction gas. The flow rate was 0.4 mL min^{-1} for Yb and 0.7 mL min^{-1} for Gd, Lu, and Nd, respectively.

The sample, after microwave-assisted digestion and evaporation using HF and boric acid, was analyzed according to the procedure described above. The calibration was performed using solutions containing all analytes in a 1.0 % v/v HNO_3 medium as a compromise condition. The figures of merit are shown in the Table 4.

The limit of detection (LOD) was calculated as 3 times the standard deviation of the analyte intensities in the blank solution (n = 10) divided by the slope of the calibration curve. The LOD values ranged from a 1.0 ng g^{-1}, for Lu and Y, to 1.1 µg g^{-1} for Sc. The relative standard deviation (RSD), that expresses the precision of the method, was evaluated by the repeatability of a set of measurements and the found values are considered acceptable, except for Yb, for REE determination by quadrupole ICP-MS, which range up to 15%.[13] The linear correlation coefficient (R) was higher than 0.9998 for all analytes.

The results for the REE determination in the certified material digested with and without HF and posterior microwave evaporation step are presented in the Table 5. The procedure without HF and determination without ammonia as reaction gas presented values in disagreement with the provided values for 7 elements (Nd, La, Pr, Eu, Dy, Sc and Y). Beside this, for those in agreement the deviations between the replicates were high. Since the sample

Table 4. Figures of merit for determination of REE in spent catalyst samples by ICP-MS, after microwave-assisted digestion and evaporation with HF with boric acid

Analyte	R	LOD / (ng g^{-1})	RSD / %
Yb[a]	0.99989	1.0	18.5
Gd[a]	0.99991	40.7	12.4
Nd[a]	0.99996	2.1	1.3
Lu[a]	0.99997	1.0	9.3
La	0.99998	81.1	0.4
Ce	0.99996	5.2	14.8
Pr	0.99995	3.3	3.5
Sm	0.99997	8.3	10.9
Eu	0.99996	3.3	1.8
Tb	0.99993	2.0	2.4
Dy	0.99997	27.3	11.1
Ho	0.99994	7.7	2.7
Er	0.99996	5.3	2.3
Tm	0.99995	2.0	3.6
Sc	0.99998	1.1[b]	8.2
Y	0.99998	14.1	9.7

[a]Values using ammonia reaction gas; [b]value in µg g^{-1}.

Table 5. Certified and obtained REE concentration values, in **µ**g g^{-1} (confidence interval 95%; n = 3), after microwave-assisted digestion with and without HF, followed by an evaporation step with boric acid for certified material TDB-1, by ICP-MS

Analyte	Certified concentration	Determined concentration without HF	Determined concentration with HF
Yb	3.4 ± 0.4	2.9 ± 0.9	2.7 ± 0.5[c]
Gd	7[a]	7.6 ± 2.1	9.7 ± 1.2[c]
Nd	23 ± 1	15.34 ± 4.0	23.4 ± 0.3[c]
Lu	0.52 ± 0.06	0.4 ± 0.1	0.75 ± 0.07[c]
La	17 ± 2	11.2 ± 3.5	17.6 ± 0.7
Ce	41 ± 4[b]	42.1 ± 6.2	41.0 ± 1.0
Pr	6[a]	3.6 ± 1.0	5.7 ± 0.2
Sm	6.0 ± 0.2	5.5 ± 1.5	6.4 ± 0.7
Eu	2.1 ± 0.1	1.2 ± 0.4	2.26 ± 0.04
Tb	1.2 ± 0.1	1.1 ± 0.3	1.25 ± 0.03
Dy	8 ± 1	5.6 ± 1.6	8.1 ± 0.9
Ho	1.3 ± 0.4	1.2 ± 0.4	1.48 ± 0.04
Er	4[a]	3.1 ± 0.9	4.3 ± 0.1
Tm	0.6 ± 0.1	0.5 ± 0.1	0.56 ± 0.02
Sc	36 ± 3	10.1 ± 4.4	41.4 ± 3.4
Y	36 ± 4	20.1 ± 5.6	31.0 ± 3.0

[a]Informed values; [b]certified value; [c]values using ammonia reaction gas.

contains high levels of silica, the digestion procedure using only HNO_3, HCl and H_2O_2 does not promote the complete decomposition of the sample, remaining after the end of the process an amount of precipitate. In fact, this procedure only promotes the extraction of the analytes from the sample, but this extraction is not as effective as demonstrated by the high deviation values.

The determinations according to the procedure developed in this work, in which the digestion is carried out with HF and with a posterior microwave-assisted evaporation step with boric acid, to accomplish the dissolution of the REE fluorides, and the use of ammonia as reaction gas, presented values in disagreement for only three elements, Gd, Lu and Y. The superiority of the procedure can also be seen by the RSD values, which were lower when compared with the values without HF and boric acid. In this procedure the use of HF is essential to achieve the complete mineralization of the sample, whose silica content is high.[15] To solubilize the REE fluorides, formed in the digestion procedure, boric acid and evaporation step were imperatives, enabling the determination of the total concentration of the analytes. The RSD values confirm this. Addition and recovery tests were performed by adding REE solution equivalent to a final concentration of 30 and 60 µg L^{-1} of the analytes to the sample before the digestion procedure in order to evaluate all steps of the method. The results presented good recoveries with values between 87% and 101%.

The use of ammonia as reaction gas to reduce polyatomic interferences was effective as can be seen in the studies performed with a reaction cell, discussed before. For two of the four elements whose determination was carried out with ammonia as reaction gas, the concentrations obtained were in agreement with the provided values for the certified material. For the other two elements, Gd and Lu, the reduction in polyatomic ions was not enough to achieve the values of the certified material. Maybe another gas would work better. Even so, the concentrations obtained for Gd and Lu were not so discrepant with the certified material, so the values for the real samples can be considered an advantageous information.

The procedure, in which 12 elements were determined without reaction cell and 4 elements using ammonia as reaction gas, was applied to ten spent catalyst samples. The results, presented as mean ± 95 % confidence interval, are shown in Table 6. The RSD for the majority of the elements were within the range up to 15 %, indicating the good precision of the method.[14] For the majority of the elements the concentration values are of the same order of magnitude that of the certified material, possibly because the material used to prepare the catalyst is from natural source. But for La, the concentration is in the range of percentage. This reveals that La is, in fact, the element used to improve the cracking characteristics of the catalyst and that a high amount is necessary. Other elements presented

Table 6. Concentration values for REE by ICP-MS (confidence interval 95%, n = 3), in ten spent catalyst samples after digestion with HF and evaporation with boric acid, assisted by microwave

Analyte	Concentration / (µg g^{-1})									
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10
Yb[a]	0.47 ± 0.01	0.59 ± 0.05	0.91 ± 0.28	0.57 ± 0.07	0.48 ± 0.09	0.69 ± 0.02	0.61 ± 0.09	0.61 ± 0.25	0.55 ± 0.07	0.62 ± 0.12
Gd[a]	24.11 ± 0.06	23.34 ± 0.36	42.42 ± 5.68	11.43 ± 1.36	10.97 ± 1.71	84.79 ± 11.66	15.42 ± 2.66	25.52 ± 5.02	12.26 ± 1.00	30.89 ± 5.41
Nd[a]	122.90 ± 0.31	129.10 ± 1.95	125.69 ± 13.61	58.19 ± 7.02	54.34 ± 7.46	108.33 ± 13.77	86.41 ± 15.28	123.0 ± 20.80	54.19 ± 4.43	157.76 ± 28.08
Lu[a]	0.11 ± 0.01	0.14 ± 0.03	0.18 ± 0.02	0.12 ± 0.05	0.09 ± 0.01	0.12 ± 0.07	0.12 ± 0.03	0.14 ± 0.05	0.13 ± 0.02	0.15 ± 0.01
La	185722 ± 46	26325 ± 403	25114 ± 960	23414 ± 3140	20550 ± 2129	30963 ± 5674	20288 ± 3248	18461 ± 3171	17827 ± 1907	33545 ± 9947
Ce	479.39 ± 1.19	314.43 ± 11.13	243.28 ± 18.95	127.07 ± 19.63	163.91 ± 19.04	214.86 ± 37.73	177.65 ± 28.74	427.51 ± 76.70	160.94 ± 15.55	501.0 ± 136.3
Pr	8.10 ± 0.02	21.99 ± 0.12	31.00 ± 2.06	8.74 ± 0.79	5.02 ± 0.58	7.20 ± 1.26	13.13 ± 2.01	10.07 ± 1.99	5.26 ± 0.64	15.83 ± 4.65
Sm	8.12 ± 0.02	13.32 ± 0.21	20.48 ± 0.34	5.33 ± 0.65	3.18 ± 0.49	16.00 ±3.30	7.03 ± 1.23	9.04 ± 2.08	5.99 ± 0.71	17.38 ± 5.73
Eu	0.48 ± 0.01	0.60 ± 0.01	0.76 ± 0.05	0.46 ± 0.05	0.37 ± 0.05	0.39 ± 0.05	0.51 ± 0.07	0.47 ± 0.08	0.40 ± 0.04	0.628 ± 0.17
Tb	0.23 ± 0.01	0.63 ± 0.01	1.02 ± 0.10	0.32 ± 0.03	0.20 ± 0.02	0.38 ± 0.06	0.40 ± 0.04	0.27 ± 0.05	0.20 ± 0.03	0.400 ± 0.13
Dy	1.09 ± 0.01	2.29 ± 0.06	3.28 ± 0.14	1.48 ± 0.21	1.01 ± 0.14	2.10 ± 0.25	1.68 ± 0.17	1.23 ± 0.35	1.02 ± 0.15	1.63 ± 0.40
Ho	0.18 ± 0.01	0.29 ± 0.02	0.40 ± 0.06	0.24 ± 0.04	0.16 ± 0.03	0.10 ± 0.01	0.23 ± 0.02	0.20 ± 0.06	0.18 ± 0.02	0.23 ± 0.04
Er	0.53 ± 0.00	0.79 ± 0.06	1.13 ± 0.09	0.71 ± 0.07	0.51 ± 0.13	1.27 ± 0.07	0.69 ± 0.06	0.60 ± 0.17	0.55 ± 0.16	0.66 ± 0.12
Tm	0.070 ± 0.007	0.07 ± 0.01	0.10 ± 0.02	0.08 ± 0.01	0.06 ± 0.01	0.035 ± 0.003	0.07 ± 0.014	0.07 ± 0.02	0.070 ± 0.006	0.07 ± 0.01
Sc	9.73 ± 0.02	6.76 ± 3.93	7.24 ± 2.89	9.42 ± 0.72	9.69 ± 0.62	16.71 ± 2.40	9.39 ± 1.24	9.82 ± 1.76	9.81 ± 0.66	9.16 ± 2.96
Y	3.44 ± 0.01	5.38 ± 0.09	8.37 ± 0.77	4.60 ± 0.49	3.14 ± 0.50	2.61 ± 0.12	4.26 ± 0.38	4.28 ± 1.15	3.67 ± 0.46	4.30 ± 0.71

[a] Concentration values obtained using ammonia as reaction gas.

considerable concentrations. The estimated abundance on the bulk of the earth for Ce and Gd are 60 µg g^{-1} and 5.4 µg g^{-1}, respectively.[14] The amount of Ce found in the spent catalyst samples ranged from 127 µg g^{-1} to 501 µg g^{-1}, about 2 to 8 times higher than the estimated abundance. For Gd, the obtained concentrations ranged from 11.4 µg g^{-1} to 84.8 µg g^{-1}, about 2 to 15 times higher than the estimated abundance. Neodymium and Sm also presented concentrations significantly higher than their estimated abundance, up to 5 times for some samples. The results of the determination show that the spent catalyst from oil refinery would have a more valuable destination if was used as a row material for REE instead of the solutions normally proposed.

Conclusions

In this work, a method for determination of 16 REE in spent catalyst sample is proposed. Three sample treatments were tested, one using HNO_3, HCl and H_2O_2 and two others using HNO_3, H_2O_2 and HF, to promote the decomposition of the silica containing compounds and an evaporation procedure with boric acid to dissolve the REE fluorides. Both, digestion and evaporation procedures, carried out with microwave assistance, made possible the determination of the total concentration of the analytes and allowed the introduction of the acid digests into the instrument without damaging the sample introduction system. Ammonia was evaluated as reaction gas in overcoming the interferences on four elements, Gd, Lu, Nd and Yb. The study showed that ammonia as reaction gas is effective in reducing polyatomic interferences. Although, only two of the four analytes had the concentration values in agreement with the provided values for the certified material, the values of the other two elements presented only a small discrepancy. It is noteworthy that the RSD achieved for the proposed method are much lower when compared with the method without the use of HF and microwave evaporation procedure. Spent catalyst samples from oil refinery contain a great amount of La and a considerable concentration of Ce, Gd and Nd, presenting a great potential as raw material for REE.

Acknowledgements

The authors are thankful to Conselho Nacional de Desenvolvimento Científico e Tecnológico (141108/2011B), CNPq, Brasília, Brazil. During the development of this work, Prof Adilson J. Curtius passed away. His contribution to this work is invaluable as well as his dedication, commitment and interest on his students and in promoting the development of science. The authors are very thankful to him.

References

1. Binnemans, K.; Jones, P. T.; Blanpain, B.; Van Gerven, T.; Yang, Y.; Walton, A.; Buchert, M.; *J. Cleaner Prod.* **2013**, *51*, 1; Suzuki, Y.; Hikida, S.; Furuta, N.; *J. Environ. Monit*. **2011**, *13*, 3420; Balaram, V.; *Trends Anal. Chem.* **1996**, *15*, 475; Massari, S.; Ruberti, M.; *Resour. Policy* **2013**, *38*, 36.
2. Alam, M. A.; Zuga, L.; Pecht, M. G.; *Ceram. Int.* **2012**, *36*, 6091.
3. Ruidong, Y.; Wei, W.; Xiaodong, Z.; Ling, L.; Huairui, W.; Miao, B.; Jingxin, W.; *J. Rare Earths* **2008**, *26*, 753; Du, X.; Graedel, T. E.; *J. Ind. Ecol.* **2011**, *15*, 836.
4. Zamorano, M.; Grindlay, A.; Molero, E.; Rodríguez, M. I.; *J. Cleaner Prod.* **2011**, *19*, 1946; Dong, T. T. T.; Lee, B.-K.; *Waste Manage.* **2009**, *29*, 1725; Koukouzas, N.; Katsiadakis, A.; Karlopoulos, E.; Kakaras, E.; *Waste Manage.* **2008** *28*, 1263.
5. Governo Brasileiro; *Política Nacional dos Resíduos Sólidos*; Lei 12.305 de 02 de agosto de 2010.
6. Hu, Z.; Zhang, W.; Liu, Y.; Chen, H.; Gaschnig, R. M.; Zong, K.; Li, M.; Gao, S.; Hu, S.; *Chem. Geol.* **2013,** *355*, 144; Gupta, J. G. S.; Bertrand, N. B.; *Talanta* **1995**, *42*, 1947; Szymczycha-Madeja, A.; Mulak, W.; *J. Hazard. Mater*. **2009**, *264*, 776; Muratli, J. M.; McManus, J.; Mix, A.; Chase, Z.; *Talanta* **2012**, *89*, 195; Hu, Z.; Gao, S.; Liu, Y.; Hu, S.; Zhao, L.; Lia, Y.; Wang, Q.; *J. Anal. At. Spectrom*. **2010**, *25*, 408.
7. García-Martinez, J.; Kunhao, L.; Krishnaiah, G.; *Chem. Commun.* **2012**, *48*, 11841; Scherzer, J.; *Appl. Catal.* **1991**, *75*, 1.
8. Cerqueira, H. S.; Caeiro, G.; Costa, L.; Ribeiro, F. R.; *J. Mol. Catal. A: Chem.*, **2008**, *292*, 1; Estevão, L. R. M.; Le Bras, M.; Delobel, R.; Nascimento, R. S. V.; *Polym. Degrad. Stab.* **2005**, *88*, 444; Chen, H-L.; Tseng, Y-S.; Hsu, K-C.; *Cem. Concr. Compos.* **2004**, *26*, 657; Marafi, M.; Stanislaus, A.; *Catal. Today* **2008**, *130*, 421; Antiohos, S. K.; Chouliara, E.; Tsimas, S.; *China Part.* **2006**, *4*, 73.
9. Houk, R. S.; Fassel, V. A.; Flesch, G. D.; Svec, H. J.; Gray, A. L.; Taylor, C. E.; *Anal. Chem.* **1980**, *52*, 2283; Tseng, Y-J.; Tsai, Y-D.; Jiang, S-J.; *Anal. Bioanal. Chem.* **2007**, *387*, 2849; Koppenaal, D. W.; Eiden, G. C.; Barinaga, J.; *J. Anal. At. Spectrom.* **2004**, *19*, 561.
10. Zawisza, B.; Pytlakowska, K.; Feist, B.; Polowniak, M.; Kita, A.; Sitko, R.; *J. Anal. At. Spectrom.* **2011**, *26*, 2373.
11. Li, X.; Dai, S.; Zhang, W.; Li, T.; Zheng, X.; Chen, W.; *Int. J. Coal Geol.* **2014**, *124*, 1; Cao, X.; Yin, M.; Wang, X.; *Spectrochim. Acta, Part B* **2001**, *56*, 431; Ardini, F.; Soggia, F.; Rugi, F.; Udisti, R.; Cubadda, G.; *Anal. Chim. Acta* **2010**, *678*, 18; Tanner, S. D.; Baranov, V. I.; Bandura, D. R.; *Spectrochim. Acta, Part B* **2002**, *58*, 1361; Raggi, A.; Coni, E.; *Anal. Bioanal. Chem.* **2006**, *384*, 887; Hattendorf, B.; Günther, D.; *J. Anal. At. Spectrom.* **2000**, *15*, 1125; Feldmann, I.; Jakubowski, N.; Stuewer, D.; *Fresenius' J. Anal. Chem.* **1999**, *365*, 415; Pick, D.; Leiterer, V.; Einax, J. W.; *Microchem. J.* **2010**, *95*, 315.

12. Alvarado, J. S.; Neal, T. J.; Smith, L. L.; Erickson, M. D.; *Anal. Chim. Acta* **1996**, *322*, 11; Kulkarni, P.; Chellam, S.; Flanagan, J. B.; Jayanty, R. K. M.; *Anal. Chim. Acta* **2007**, *599*, 170; Kulkarni, P.; Chellam, S.; Mittlefehldt, D. W.; *Anal. Chim. Acta* **2007**, *581*, 247; Navarro, M. S.; Andrade, S.; Ulbrich, H.; Gomes, C. B.; Girardi, V. A. V.; *Geostand.Geoanal. Res.* **2008**, *32*, 167; Fedyunina, N. N.; Seregina, I. F.; Bolshov, M. A.; Okina, O. I.; Lyapunov, S. M.; *Anal. Chim. Acta* **2012**, *713*, 97.
13. Rousseau, T. C. C.; Sonke, J. E.; Chmeleff, J.; Candaudap, F.; Lacan, F.; Boaventura, G.; Seyler, P.; Jeandel, C.; *J. Anal. At. Spectrom.* **2013**, *28*, 573.
14. Henderson, P.; *Developments in Geochemistry 2 - Rare Earth Element Geochemistry*, 1st ed.; Elsevier Science Publishers B.V.: New York, 1984.
15. Sastre, J.; Sahuquillo, A.; Vidal, M.; Rauret, G.; *Anal. Chim. Acta* **2002**, *462*, 59; Low, F.; Zhang, L.; *Talanta* **2012**, *101*, 346.

Submitted on: January 11, 2014

Published online: April 16, 2014