Determination of Fe and Ca in Alumina-based Nickel-Molybdenum Hydrodesulphurization Catalysts Using Inductively Coupled Plasma Optical Emission Spectrometry and Inductively Coupled Plasma Dynamic Reaction Cell Mass Spectrometry

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ABSTRACT

The analytical performance of inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) for the determination of Fe and Ca in alumina-based nickel-molybdenum hydrodesulphurization catalysts was evaluated. Although the typical concentration of both elements is quite high (0.02–0.4% for Fe and 0.02–0.2% for Ca), the complex matrix of the catalysts strongly influences the results. Before measurements, effective digestion using $\text{HClO}_4 + \text{HF}$, H_3BO_3 , and HCl was executed.

The accuracy of the results was evaluated by spiking a raw catalyst sample before digestion and measuring the recoveries. In the case of ICP-OES, a 10-fold dilution of the sample digest solution yielded recoveries of 95% for

Fe and 102% for Ca. In the case of ICP-MS, the use of dynamic reaction cell (DRC) with ammonia as a reaction gas along with the low mass bandpass was crucial. The optimized ICP-DRC-MS conditions were as follows: ^{56}Fe and ^{42}Ca as monitored isotopes, ammonia flow rate of 0.45 mL min^{-1} , RPa of 0.00 and RPq of 0.65 mL min^{-1} . Applying these conditions, the recovery was 97% for Fe and 89% for Ca, and the results of ICP-OES and ICP-MS were in satisfactory agreement. As no appropriate reference materials are available, cross-validation of both methods turned out to be a crucial tool for confirmation of the accuracy of the results. This work also shows that the use of DRC is an effective way for spectral interference elimination in a complex matrix.

The determination of Fe and Ca in environmental, biological, and industrial materials is a frequent and routine analytical task. However, literature concerning the determination of the metals in various petroleum industry catalysts is poor. Iron was determined in alumina-silicate-based catalysts (3-7), in alumina-based reforming or automotive catalysts containing noble metal (7-9), as well as in spent hydrodesulphurization (10) and in various heterogeneous catalysts (11). Determination of Ca in the samples is rarer (7). Some data dealing with materials similar to the Ni-Mo/ Al_2O_3 catalysts can also be useful, in particular when alumina, one of the widely used ceramic materials, is concerned (12-26). The common approach to alumina or catalyst analysis is acid digestion followed by metal determination using flame atomic absorption spectrometry (FAAS) (3-6,9,11), microwave-induced plasma optical emission spectrometry (MIP-OES) (16), inductively coupled plasma optical emission spectrometry (ICP-OES) (3,7,10-15,19,24) or inductively coupled plasma mass spectrometry (ICP-MS) (8,17,18,22,25). Some papers report direct (or slurry) alumina analysis (14, 20-23,26), often with electrothermal sample vaporization to plasma (20-22).

To the best of our knowledge, so far no data have been published on the determination of iron and calcium impurities in Ni-Mo/ Al_2O_3

INTRODUCTION

Iron and calcium are well known poisons to catalysts composed of nickel-molybdenum supported on alumina used for hydrosulphurization of heavy petroleum products. Their content in the catalysts is an

important factor influencing technological decisions, which results in more economic work of industrial units and reduction in the amount of hazardous wastes (1,2). Typically, the catalyst contains heavy petroleum oil, as well as Al, V, Ni, Mo, S, Na (up to 40, 33, 16, 4, 11, 8, and 1%, respectively), and Zn, Cl, Si, Ti, P, As, Cu, Co (all below 0.01%). The concentration of Fe and Ca lies in the range of 0.02–0.4 % and 0.02–0.2 %, respectively.

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hydrotreating catalysts. The main aim of this work was evaluation of the analytical performance of ICP-OES and ICP-QMS for the determination of Fe and Ca in Ni-Mo/Al₂O₃ hydrotreating catalysts after their acid decomposition.

ICP-OES seems to be a suitable analytical technique for Fe and Ca determination at moderate concentration levels (3,7,10). However, the complex matrix of hydrotreating catalysts can cause interferences; thus, its influence on the accuracy of the results should be checked. As was pointed out in the comprehensive review by Todoli et al. (27), matrix components impact many physico-chemical processes and can change, among others, the quality of the aerosol produced by nebulization of the sample, thermal conditions in the plasma, the state in which an analyte and potential interfering species are introduced to the plasma, and their excitation efficiency and spatial distribution.

The matrix influence on processes occurring in the sample introduction system and in the inductively coupled plasma are also concerns for ICP-MS, but because of lower detection limits and higher sample dilution, a decrease of physico-chemical effects is possible. The disadvantage of ICP-MS is a higher susceptibility to spectral interferences. Fe and Ca are known as difficult elements for MS since detection of their main isotopes ⁵⁶Fe (91.7% abundance) and ⁴⁰Ca (96.9% abundance) is strongly influenced by the polyatomic ion ⁴⁰Ar¹⁶O⁺ and the argon ion ⁴⁰Ar⁺, respectively (28,29). Determination of these main isotopes can lead to overestimation of the results if the spectral interferences are not corrected (8,30). The less abundant isotopes [⁵⁴Fe (30-33), ⁵⁷Fe (17,20,30,31,24), ⁴²Ca (34), ⁴³Ca (34), and ⁴⁴Ca (32)] are sometimes used for the determination of iron and calcium. Another approach is the use

of high resolution ICP-MS. A medium resolution of 3000 was found to be sufficient in order to distinguish masses of the main iron isotope, ⁵⁶Fe, and the polyatomic ion ⁴⁰Ar¹⁶O⁺ (18,30,33,35). Introduction of a sample into an ICP-MS by electrothermal vaporization or after membrane desolvation was regarded as beneficial, as this leads to considerably less oxygen introduction into the ICP (18,20,22,36). Application of "cool plasma" conditions can decrease the formation of argon-based polyatomic ions generated within the plasma, but under such conditions matrix effects are usually more severe (36-38). Some authors reported the detrimental interferences caused by polyatomic ions containing the ⁴⁰Ca isotope: ⁴⁰Ca¹⁶O⁺ and ⁴⁰Ca¹⁶OH⁺ on ⁵⁶Fe and ⁵⁷Fe determination, respectively (35-39). Baker et al. used a mathematical correction to overcome the effect of the ⁴⁰Ca¹⁶OH⁺ ion on the ⁵⁷Fe isotope determination (34) by measuring the intensities of ⁴³Ca⁺ and ⁴³Ca¹⁶OH⁺. Mathematical corrections were also applied by Ingle et al. (41). They used the signal of the ⁵³Cr isotope to correct the results of the ⁵⁴Fe determination in the presence of ⁵⁴Cr [otherwise the required resolution is 73,900 (36)], and the signal of ⁶⁰Ni for the correction of the ⁵⁸Fe determination in the presence of ⁵⁸Ni [otherwise the required resolution is 28,000 (36)]. Matrix removal and analyte preconcentration can be effective in minimizing spectral interferences (18,38,42). Application of ditiocarbamate (18), desferrioxamine chelation agent (42), or silica-immobilized 8-hydroxy-quinoline (38) was reported for the elimination of the influence of the aforementioned polyatomic ions containing ⁴⁰Ca isotope on the iron determination.

The powerful, although still not widely explored, tool for elimination of spectral interferences is the use of reaction/collision cells to convert interfering species into

non-interfering products, owing to ion-molecule reactions with the use of a gas within the cell (29,43-47). The requirement is that new species, appearing as a consequence of reactions ongoing in the cell, do not interfere with the measured isotopes. In another case, post-cell kinetic energy discrimination and in-cell bandpass tuning could be used to decrease the influence of side products (43-47). Various reaction/collision cell configurations have already been used for the determination of ⁵⁶Fe and ⁴⁰Ca isotopes. Ammonia (36-40,44,48-53), methane (52), carbon monoxide (36), or nitrogen (36) were used as reaction gases in quadrupole ICP-MS. The materials analyzed were, among others, high purity acids and hydrogen peroxide from the semiconductor industry, glass, rice, and human serum. The ⁵⁶Fe isotope was also measured in moss samples (52) and foodstuff of animal origin (53) using a hexapole collision cell with mixtures of hydrogen and helium as cell gas. The use of hydrogen was not completely effective in the determination of the ⁵⁶Fe and ⁵⁷Fe isotopes in calcium-rich water; therefore, a suppressor column was additionally applied (54).

The common mode of reactive gas application is removal of interferences by influence on interfering ions. Another idea would be chemical separation by moving the analyte mass of interest (39,45). Cluster ion formation in the reaction of Fe ions with NH₃ (Fe(NH₃)_n⁺), C₂H₄ (Fe(C₂H₄)⁺), NO₂, and NO (FeO⁺) was reported; however, this was not as analytically beneficial (39,45). The formation of clusters with ammonia was not observed in case of the Ca ion (45).

To the best of our knowledge, no paper dedicated to the determination of Fe and Ca in Ni-Mo/Al₂O₃ hydrotreating catalysts by ICP-MS has been published, and the litera-

ture devoted to the application of ICP-OES for various catalyst analyses is very scarce. It should be stressed that in the investigated analytical case it was not possible to apply common validation scenarios because of the lack of appropriate certified reference materials, proficiency tests, or inter-laboratory comparisons. Therefore, our effort was focused on the optimization of the analytical protocol for both ICP-OES and ICP-MS so as to be able to compare the results and cross-validate both analytical procedures.

EXPERIMENTAL

Instrumentation and Experimental Conditions

A JY 70 Plus Geoplasma ICP-OES spectrometer (Jobin-Yvon, France) with a high resolution 1-m Czerny-Turner monochromator, equipped with a 50 cm long Roland circle Paschen-Runge polychromator, was used; the conditions are listed in Table I. The wavelengths of 259.940 nm for Fe and 317.933 nm for Ca were selected. According to the resolution test, the resolution at 228.616 nm (Co line) was better than 0.009 nm, and the resolution at 310.030 nm (Fe line) was better than 0.006 nm.

An ELAN® DRC™ 6100 quadrupole ICP-MS (PerkinElmer, Shelton, CT, USA), equipped with cyclonic type spray chamber and Meinhard® nebulizer (Table I), was used for the ICP-MS measurements.

A muffle furnace Carbolite CWF 1200 (Sheffield, Great Britain), a Soxhlet apparatus for extraction (Buchi, Switzerland), and a Pulverisette 7 mill with agate dish and balls (Fritsch, Germany) as well as platinum crucibles were used for sample preparation.

Reagents and Materials

A CertiPUR® multielement standard containing, among others, 100 mg L⁻¹ of Fe and 1000 mg L⁻¹ Ca

(E. Merck, Darmstadt, Germany), was used for the calibration of both the ICP-OES and ICP-MS.

Iron oxide(III) (Johnson Matthey Ltd., Great Britain) and calcium carbonate(II) (Aldrich Chemical Co., USA) were used for spiking the raw catalyst samples.

Inorganic acids used in this work were: hydrochloric (d=1.19 g mL⁻¹), hydrofluoric (d=1.16 g mL⁻¹), perchloric (d=1.60 g mL⁻¹), and boric acid (all acids were obtained from POCh, Gliwice, Poland).

All reagents were at least of analytical grade.

Samples

Alumina-based nickel-molybdenum catalysts were taken from industrial units of heavy petroleum product hydrodesulphurization. Fresh and spent catalysts of various degrees of wear were selected. For the recovery experiments, known amounts of iron oxide(III) and calcium carbonate(II) were added to

the raw industrial samples before execution of the digestion process.

Sample Preparation

The raw catalyst samples were first washed to remove oil residue from the industrial process by extraction with toluene in a Soxhlet apparatus. Then the catalysts were ground in an agate ball mill, weighed into platinum crucibles, and burnt in a muffle furnace at 500 °C. The obtained ash was dissolved on a hot plate using the 3-step procedure with the following reagents added sequentially: (i) 3 mL concentrated HF + 3 mL concentrated HClO₄; (ii) 3 mL 4% H₃BO₃; and (iii) 5 mL concentrated HCl, all under a conventional fume hood. The acids were always added to the cold samples (outside the hot plate). The temperature of the hot plate was not measured, but the heating temperature was kept very low just to achieve slow evaporation of the solution. The heating time lasted up to a few hours at which evaporation of the solution

TABLE I
ICP-OES and ICP-MS Operating Conditions

	ICP-OES	ICP-MS
RF power	1.0 kW	1.1 kW
Plasma gas flow rate	12.0 L min ⁻¹	15.5 L min ⁻¹
Intermediate gas flow rate	0.2 L min ⁻¹	1.25 L min ⁻¹
Nebulizer	Cross flow	Meinhard®
Nebulizer gas flow rate	0.35 L min ⁻¹ (2.6 bar)	0.94 L min ⁻¹
Observation height above coil	15 mm	-
Sample uptake rate	1.0 mL min ⁻¹	1.5 mL min ⁻¹ (peristaltic pump 20.0 rpm)
Integration time	3 sec	0.6 sec
Detector mode	-	Dual
Scanning mode	-	Peak hopping
Reading per replicat	-	1
Sweeps per reading	-	6
Number of replicates	-	5
Dwell time	-	100 ms

was near dryness (in each step). With this procedure, it was possible to transfer around 0.1 – 0.3 g of the catalyst to 25 mL in the final solution of HCl 1:5 (v:v). The samples were prepared in triplicate.

In the recovery experiments, the known amounts of iron and calcium compounds were added to the catalyst after Soxhlet extraction. Then, the mixing was executed in a ball mill for over 20 minutes. The spiked and non-spiked catalyst samples underwent the same analytical procedure.

RESULTS AND DISCUSSION

Analytical Performance of ICP-OES

The optimized experimental conditions for ICP-OES in the determination of Fe and Ca are listed in Table I. The effects of possible interferences from the catalyst matrix were investigated by analyzing the solution containing: 3000 mg kg⁻¹ of Al, 1000 mg kg⁻¹ of V, 600 mg kg⁻¹ of S, 500 mg kg⁻¹ of Mo, 400 mg kg⁻¹ of Ni, and 100 mg kg⁻¹ of Na. Two effects could have been expected: (i) those coming from the spectral interferences and (ii) those coming from the physico-chemical phenomena. In terms of the first case, careful examination in the vicinity of the selected Fe and Ca emission lines (259.940 nm and 317.933 nm, respectively) was performed. No spectral interferences were detected when solutions of heavy wear catalysts were analyzed. In order to evaluate the physico-chemical effects, the solution obtained after digestion (sample dilution related to the raw catalyst 1:100, v:v) was introduced into the plasma directly or after 10-fold further dilution (sample dilution related to raw catalyst 1:1000, v:v) in the solution of HCl (1:5, v:v). It can be seen in Table II that higher dilution leads to recoveries closer to 100%, while lower dilutions resulted in lower recover-

ies. Since the blank was strictly controlled, the underestimation of the results obtained at lower dilution must result from matrix suppression. This assumption was confirmed by the recovery experiments. The recovery values were closer to 100% at higher dilution. Finally, 1:1000 dilution of the raw sample was selected to overcome interferences in the ICP-OES analysis.

Analytical Performance of ICP-QMS

Although it was possible to obtain satisfactory recoveries with ICP-OES, ICP-MS was also used to validate the results. The experimental conditions for the ICP-MS measurements are listed in Table I. Because of the limited resolution of a quadrupole analyzer, proper selection of the isotopes was crucial. This was done by careful examination of isotope abundance and potential interfering ions that can be formed in the plasma when

a catalyst solution is introduced (Table III).

Owing to high concentrations of several matrix elements present in the catalyst, a dilution factor of 1:5000 (m:v) was used. Thus, for the measurement of Fe and Ca, the isotopes with higher abundances are more appropriate; thus, the ⁵⁸Fe, ⁴³Ca, ⁴⁶Ca, and ⁴⁸Ca isotopes were measured. Additionally, the influence of ⁵⁸Ni on ⁵⁸Fe, ²⁷Al¹⁶O⁺ on ⁴³Ca, and ³²S¹⁶O⁺ on ⁴⁸Ca could have been expected in cases when the samples contained nickel, aluminum, and sulfur at percentage levels.

At the first instance, the moderately abundant ⁵⁴Fe, ⁵⁷Fe, and ⁴⁴Ca isotopes were selected for ICP-MS measurement without DRC usage. Although the recovery for the spiked samples was satisfactory (112%, 105%, and 109% for ⁵⁴Fe, ⁵⁷Fe, and ⁴⁴Ca, respectively), huge discrepancies between the ICP-MS and ICP-OES results were observed

TABLE II
Recovery in ICP-OES Analysis

Element	Sample No.	Sample Dilution	Analysis Result ± SD (%) Sample	Standard	Recovery (%)
Fe	1 ^a	1: 100 ^a	0.016 ± 0.002	0.092 ± 0.006	75
		1: 1000	0.026 ± 0.001	0.113 ± 0.001	95
	2	1: 100	0.016 ± 0.002	0.179 ± 0.004	79
		1: 1000	0.026 ± 0.001	0.214 ± 0.005	103
	3	1: 100	0.141 ± 0.007	0.234 ± 0.008	81
		1: 1000	0.168 ± 0.008	0.279 ± 0.005	89
	4	1: 1000	0.143 ± 0.003	0.307 ± 0.008	98
		1: 1000	0.048 ± 0.002	0.166 ± 0.004	88
	Ca	1: 100 ^a	0.040 ± 0.003	0.099 ± 0.006	82
		1: 1000	0.075 ± 0.007	0.161 ± 0.012	106
	2	1: 100	0.040 ± 0.003	0.196 ± 0.003	84
		1: 1000	0.075 ± 0.007	0.260 ± 0.015	99
	3	1: 100	0.052 ± 0.002	0.185 ± 0.004	82
		1: 1000	0.075 ± 0.017	0.260 ± 0.020	104
	4	1: 1000	0.122 ± 0.009	0.253 ± 0.009	99
		1: 1000	0.051 ± 0.003	0.252 ± 0.012	103

^a Fresh catalysts.

TABLE III
Data for Isotope Selection

Atomic No.	Abundance (%)	Mass Overlapping Ions	Selection for Analysis by	
			ICP-MS	ICP-DRC-MS
Fe				
54	5.845	⁴⁰ Ar ¹⁴ N ⁺ , ³⁷ Cl ¹⁶ O ¹ H ⁺ , ³⁸ Ar ¹⁵ N ¹ H ⁺ , ³⁶ Ar ¹⁸ O ⁺ , ³⁸ Ar ¹⁶ O ⁺ , ³⁶ Ar ¹⁷ O ¹ H ⁺ , ³⁶ S ¹⁸ O ⁺ , ³⁵ Cl ¹⁸ O ¹ H ⁺ , ³⁷ Cl ¹⁷ O ⁺ , ⁵⁴ Cr ⁺	+	-
56	91.754	⁴⁰ Ar ¹⁶ O ⁺ , ³⁸ Ar ¹⁸ O ⁺ , ⁴⁰ Ca ¹⁶ O ⁺ , ⁴⁰ Ar ¹⁵ N ¹ H ⁺ , ³⁸ Ar ¹⁷ O ¹ H ⁺ , ³⁷ Cl ¹⁸ O ¹ H ⁺ , ¹¹² Cd ²⁺	-	+
57	2.119	⁴⁰ Ar ¹⁶ O ¹ H ⁺ , ⁴⁰ Ca ¹⁶ O ¹ H ⁺ , ⁴⁰ Ar ¹⁷ O ⁺ , ⁴⁰ Ca ¹⁷ O ⁺ , ⁴¹ K ¹⁶ O ⁺ , ³⁸ Ar ¹⁸ O ¹ H ⁺ , ⁴⁰ Ar ¹⁷ O ¹ H ⁺ , ¹¹⁴ Cd ²⁺	+	-
58	0.282	⁴⁰ Ar ¹⁸ O, ⁴⁰ Ar ¹⁷ O ¹ H, ⁴⁰ Ca ¹⁸ O ⁺ , ⁴² Ca ¹⁶ O ⁺ , ²³ Na ³⁵ Cl ⁺ , ⁵⁸ Ni ⁺	-	-
Ca				
40	96.941	⁴⁰ Ar ⁺	-	+
42	0.647	⁴⁰ Ar ¹ H ₂ ⁺ , ²⁶ Mg ¹⁶ O ⁺ , ¹⁴ N ₃ ⁺	+	+
43	0.130	²⁷ Al ¹⁶ O ⁺ , ⁸⁶ Sr ⁺	-	-
44	2.086	¹² C ¹⁶ O ₂ ⁺ , ¹⁴ N ₂ ¹⁶ O ⁺ , ²⁸ Si ¹⁶ O ⁺ , ⁸⁸ Sr ²⁺ , ²⁷ Al ¹⁶ OH ⁺	+	-
46	0.004	¹⁴ N ¹⁶ O ₂ ⁺ , ³² S ¹⁴ N ⁺ , ²⁸ Si ¹⁸ O ⁺ , ⁴⁶ Ti ⁺ , ¹² C ¹⁶ O ¹⁸ O ⁺	-	-
48	0.187	³⁶ Ar ¹² C ⁺ , ¹⁴ N ¹⁶ O ¹⁸ O ⁺ , ³³ S ¹⁵ N ⁺ , ³⁴ S ¹⁴ N ⁺ , ³² S ¹⁶ O ⁺ , ⁴⁸ Ti ⁺	-	-

TABLE IV
Recovery in ICP-MS Analysis

Analytical Conditions and Technique	Analysis Results $\pm$ SD (%)				
	Sample	ICP-MS relative to ICP-OES results (%)	Sample Spiked	ICP-MS relative to ICP-OES results (%)	Recovery (%)
Fe determination					
ICP-OES	0.160 $\pm$ 0.006	–	0.335 $\pm$ 0.005	–	97
ICP-MS, ⁵⁴ Fe	0.235 $\pm$ 0.008	147	0.462 $\pm$ 0.016	140	112
ICP-MS, ⁵⁷ Fe	0.203 $\pm$ 0.014	127	0.403 $\pm$ 0.018	135	105
ICP-MS, ⁵⁶ Fe, DRC, RPa=0.0, RPq=0.25	0.206 $\pm$ 0.007	129	0.591 $\pm$ 0.015	176	154
ICP-MS, ⁵⁶ Fe, DRC, RPa=0.0, RPq=0.45	0.171 $\pm$ 0.008	107	0.318 $\pm$ 0.013	95	90
ICP-MS, ⁵⁶ Fe, DRC, Rpa=0.0, RPq=0.65	0.176 $\pm$ 0.010	110	0.348 $\pm$ 0.013	104	97
Ca determination					
ICP-OES	0.089 $\pm$ 0.008	–	0.236 $\pm$ 0.010	–	95
ICP-MS, ⁴⁴ Ca	0.260 $\pm$ 0.010	292	0.448 $\pm$ 0.016	190	109
ICP-MS, ⁴² Ca, DRC, RPa=0.00, RPq=0.25	0.197 $\pm$ 0.012	221	0.439 $\pm$ 0.014	86	124
ICP-MS, ⁴² Ca, DRC, RPa=0.00, RPq=0.45	0.153 $\pm$ 0.008	172	0.241 $\pm$ 0.010	102	77
ICP-MS, ⁴² Ca, DRC, RPa=0.00, RPq=0.65	0.098 $\pm$ 0.005	110	0.227 $\pm$ 0.012	96	87

(Table IV). This indicates that even though the recoveries of the spiked samples were within an acceptable range for both analytical techniques (ICP-OES and ICP-MS), the results differ to such an extent that it is not possible to judge which one of them is accurate. This makes it clear that judgment based only on the recovery test could lead to false results and, thus, cannot be perceived as sufficient to evaluate the quality of the results in the considered analytical case. With interferences more pronounced in ICP-MS measurements, it was decided to focus on the evaluation of this technique's analytical conditions. An attempt was made to use the most abundant isotopes, ^{56}Fe and ^{40}Ca , with the application of the dynamic reaction cell to eliminate spectral interferences (Table III).

According to the literature, ammonia is an effective reaction gas for the determination of Fe and Ca in various samples (36-40,43,45,48-50); therefore, it was selected for this work. The effect of ammonia flow rate on the signal intensities of ^{56}Fe and ^{40}Ca was investigated for the blank solution, for the wear catalyst solution, as well as for the standard solution (Figures 1-3).

As can be seen in Figure 1, the decrease of blank signal with an increase in ammonia flow rate, regarded as the $^{40}\text{Ar}^{16}\text{O}^+$ effect, was observed, while the decrease of the $^{56}\text{Fe}^+$ signal in the case of the catalyst and standard solutions was much lower. The criteria for the selection of ammonia flow rate were both the lowest intensity of the blank solution and the biggest difference between intensity of blank and standard solution. Finally, the selected flow rate of ammonia was equal to 0.45 mL min^{-1} in the ^{56}Fe determination.

When ^{40}Ca was monitored, an increase in the ammonia flow rate

significantly decreased both the blank and the analyte ion signals (Figure 2), meaning that it is not possible to overcome the interferences in the applied conditions (ammonia flow rate below 0.8 mL min^{-1} ; bandpass boundaries not applied). At last, although sacrificing the sensitivity, the lower abundant isotope, ^{42}Ca , was also examined (Figure 3). In this case it was possible to find optimal conditions with the flow rate of NH_3 at 0.45 mL min^{-1} , the same as for ^{56}Fe . In all further experiments, the flow rate of NH_3 was settled to 0.45 mL min^{-1} .

Fig. 1. Ammonia flow rate optimization for the determination of ^{56}Fe isotope.

Fig. 2. Ammonia flow rate optimization for the determination of ^{40}Ca isotope

Fig. 3. Ammonia flow rate optimization for the determination of ^{42}Ca isotope.

Besides the optimization of the ammonia flow rate, the efficiency of the DRC™ depends on the band-pass boundaries. Those are defined by the rejection (Mathieu) parameters “q” (RPq) and “a” (RPa), indicating the low and high mass cut parameters, respectively (43,45, 47). The proper choice of rejection parameters prevents unwanted precursors of new interfering species, which could form in the presence of a reactive gas. The optimization of the experimental parameters was performed with RPa set to “0.00”, and by varying the value of RPq. With the increase of RPq value, better recovery was obtained. Using RPa of 0.00 and RPq of 0.65, the recovery was 97% for ⁵⁶Fe and 89% for ⁴²Ca, which was satisfactory; moreover, good agreement between the results of ICP-MS and ICP-OES was finally achieved.

The overestimation of the results obtained for the ⁵⁴Fe, ⁵⁷Fe, and ⁴⁴Ca isotopes in the preliminary experiments was probably caused by the interfering polyatomic ions ⁴⁰Ar¹⁴N⁺ for ⁵⁴Fe, ⁴⁰Ar¹⁶OH⁺ or ⁴⁰Ca¹⁶OH⁺ for ⁵⁷Fe, and ¹²C¹⁶O₂⁺ or ²⁷Al¹⁶OH⁺ for ⁴⁴Ca. Although ammonia was reported as an efficient gas to remove spectral effects also in the determination of ⁵⁴Fe and ⁵⁷Fe (34), the satisfactory results obtained for ⁵⁶Fe and ⁴²Ca isotopes made further efforts unnecessary.

The polyatomic nitrogen ion ¹⁴N₃⁺ is shown in Table III as a potential interference on ⁴²Ca; however, this ion was not observed during the experiments performed here. Other authors report that ¹⁴N₃⁺ was formed from the N₂ molecule (nitrogen used in a desolvation system) but was not formed when solutions containing nitric acid were measured (52).

Figures of Merit

The detection limits of both applied analytical methods were calculated as three standard devia-

tions of the measurement results of six procedural blank solutions (blank for the whole analytical procedure, including sample preparation steps). The detection limits were further recalculated for the raw catalyst material taking into account the applied dissolution of the original sample. The results are summarized in Table V. Although ICP-MS offers lower detection limits for the direct determination of Fe and Ca in the final solution, the difference is much less pronounced when the dilution factor is considered, as can be seen for the detection limits calculated for the raw sample. The obtained detection limits of both methods are sufficiently low with regard to the determination of Fe and Ca impurities in the catalysts. Lowering the detection limits was not the aim of this work, in contrast to some other applications, e.g., high-purity alumina analysis (12,14,15). The most important issue from a technological point of view is the accuracy of the results for the Fe and Ca determination in wear catalysts since this influences the production process. This was assured by opti-

mization of the experimental parameters of both ICP-OES and ICP-MS.

Considering the lack of spectral interferences, ICP-OES was used as the method of choice, and the accuracy of the results was verified by the use of ICP-MS with DRC. It should be stressed that the selection of the optimized conditions for ICP-MS required much more effort due to serious spectral interferences. The good agreement of the results obtained by ICP-OES and ICP-MS validates both measurement techniques. For routine application, ICP-OES is recommended because of its lower cost and ease of use for this application.

The sample preparation step was positively verified by the recovery in the whole analytical procedure. Using the selected analysis conditions, the recovery (Tables II and IV, n=7) was 88–103% (95% on average) for Fe and 87–106% (99% on average) for Ca.

TABLE V
Detection Limits of Analytical Procedure

Analytical Conditions and Technique	Detection Limit of Analytical Procedure	
	For final solution (mg L ⁻¹)	For raw catalyst sample (%)
Fe determination		
ICP-OES	0.066	0.0066
ICP-MS	0.0048	0.0024
(⁵⁶ Fe, DRC, 0.45 mL min ⁻¹ NH ₃ , RPa=0.00, RPq=0.65)		
Ca determination		
ICP-OES	0.23	0.023
ICP-MS	0.0082	0.0041
(⁴² Ca, DRC, 0.45 mL min ⁻¹ NH ₃ , RPa=0.00, RPq=0.65)		

CONCLUSION

Analytical procedures for the accurate determination of industrially important Fe and Ca in dissolved Ni-Mo/Al₂O₃ hydrotreating catalysts by use of ICP-OES or ICP-DRC-MS were proposed. In the case of ICP-OES, no spectral interferences were detected, and the observed signal suppression (a physico-chemical effect) was eliminated by appropriate dilution of the digest solution, whereas with ICP-MS serious spectral interferences appear requiring the use of the DRC with ammonia as a reactive gas for the elimination of interfering species. Both techniques achieved good recovery for the sample spiked with Ca and Fe under optimized conditions. In spite of good recovery, the results obtained for industrial catalysts using both methods differed significantly. Careful optimization of rejection parameters of mass filter turned out to be necessary to filter out secondary interfering species with ICP-MS.

Taking into account that in the case of the determination of Fe and Ca in Ni-Mo/Al₂O₃ hydrotreating catalysts, neither certified reference materials nor inter-laboratory comparisons/proficiency testing were available, the simultaneous execution of the recovery test and the cross-comparison of the results obtained by the two analytical techniques was crucial for evaluating the accuracy of the results.

For the routine determination of Ca and Fe in the catalyst of interest, ICP-OES would be recommended. ICP-MS, applied here for validation purposes, could be a method of choice in future work for the determination of other elements present at much lower concentrations.

The essential finding of the work is that judgment based only on the recovery test can lead to false conclusions and cannot be considered

as sufficient evaluation of the quality of the results.

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