Determination of Ni and Cr in oil samples by isotope dilution applied to aqueous and organic matrices using ICP-MS

Laís N. Viana (PG)[1], Tatiana D. Saint'Pierre* (PQ)[1]

[1]Pontifícia Universidade Católica do Rio de Janeiro, Departamento de Química, Rio de janeiro, RJ, Brasil, 22451-900[a]
**e-mail: tatispierre@puc-rio.br*

Keywords: *Ni, Cr, isotope dilution, ICP-MS*

Introduction

Trace metals present in oil samples can be responsible for catalyze reactions that can result in corrosion of engine parts, catalyst poisoning, or fuel degradation.[1,2] The quantification of metals in oil samples is important for obtaining relevant information, application of corrective measures to guarantee the quality of refined products, and evaluation of the environmental impact of oil production and usage.[3,4] Inductively coupled plasma mass spectrometry (ICP-MS) shows to be a robust and reliable technique for trace elements determination, with high sensitivity for multielemental analysis, and capability of isotopic-ratio measurments.[4,5] The aim of this work is the development and comparison of methods for determination of Ni and Cr in petroleum asphalt cement (CAP) by isotope dilution (ID) applied to aqueous and organic matrices using ICP-MS.

Results and Discussion

The standard reference material NIST SRM 1084a (wear-metals in lubricant oil) was used for accuracy evaluation. Oil samples were analyzed after direct dilution in a mixture of xylene and butanol in the 60:40 ratio, and after acid decomposition with 2.5 mL of HNO_3 and 1.0 mL of H_2O_2 in a digestion block. The isotopic materials were added directly into the organic solutions, and prior to the acid decompositions. For introduction of organic samples in the ICP-MS a Meinhard nebulizer coupled to a cryogenic desolvation unit kept at -5 °C was used. Oxygen was introduced as auxiliary gas to avoid carbon deposits on cones and lenses. RF power and nebulizer gas flow rate were optimized for each method. To overcome the spectral interference of $^{40}Ar^{12}C^+$ over ^{52}Cr, a dynamic reaction cell with CH_4 as reaction gas was used. Detection and quantification limits are shown in Table 1.

Table 1. Instrumental LD and method LQ.

Method	LD (µg L^{-1})		LQ (µg kg^{-1})	
	Ni	Cr	Ni	Cr
Aqueous ID	0.44	0.31	232	164
Organic ID	0.22	0.48	116	253

Concentrations obtained for the certified reference material and for the oil sample using both methods are presented in Tables 2 and 3.

Table 2. Concentrations, in mg $kg^{-1,}$ found for Ni and Cr in the CRM by both methods.

Method	Ni	Cr
Certified values	99.7 ± 1.6	98.3 ± 0.8
Aqueous ID	84.9 ± 3.1	87.2 ± 3.6
Organic ID	100.4 ± 1.1	117 ± 0.8

Table 3. Ni and Cr concentrations found in oil sample for both methods, in mg kg^{-1}.

Method	Ni	Cr
Aqueous ID	40.6 ± 1.4	2.0 ± 0.08
Organic ID	40.7 ± 1.0	1.8 ± 0.04

The recoveries obtained were within the range of 85 % to 120 %, confirming the accuracy of the method. The RSDs were lower than 3 % for organic isotope dilution, and 5 % for aqueous isotope dilution, indicating precision of the applied methods.

Conclusions

Both methods demonstrated efficiency in the determination of Ni and Cr in oil samples. The CH_4 as reaction gas allowed reducing the interference over ^{52}Cr. The successful application of isotope dilution in organic solutions is a very promising result and the great differential of this work.

Acknowledgments

CAPES CNPq FAPERJ PUC RIO

[1]Donati GL, Amais RS, Schiavo D, Nóbrega JA, J. of Anal. At. Spectrom., **2013**, 28, 755.
[2]Kumar SJ, Gangadharan S, J. of Anal. At. Spectrom., **1999**, 14, 967.
[3]Duyck CB, Miekeley N, da Silveira CLP, Szatmari P, Spectrochim. Acta, Part B, **2002**, 57, 1979.
[4]Ammann AA, J. of Mass Spectrom., **2007**, 42, 419.
[5]Heilmann, Boulyga SF, Heumann G, J. of Anal.l At. Spectrom., **2009**, 24, 385.