DIRECT DETERMINATION OF Ni AND Cr IN OIL SAMPLES BY ISOTOPE DILUTION USING ICP-MS

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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] For example, the content of nickel, along with vanadium, in oil samples can be used for oil classification and for information about maturation, geological origin and migration of crude oil, which are aspects of high significance for exploration processes.[5,6] 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.[4,6] The aim of this work is the development of a method for direct determination of Ni e Cr in petroleum asphalt cement (CAP) samples by isotope dilution using ICP-MS. For comparison purposes, an external calibration method was also performed. Calibration and sample solutions were prepared in a 60/40 (v/v) xylene/butanol mixture. The standard reference material NIST SRM 1084a (wear-metals in lubricant oil) was used for method validation. Six-point calibration curves were prepared with concentrations varying from 1.0 to 80.0 μg kg^{-1} using the Conostan S-21 standard. The ^{60}Ni and ^{52}Cr isotopes were measured in the external calibration method, and the isotope ratios $^{61}Ni/^{60}Ni$ and $^{50}Cr/^{52}Cr$ were analyzed by isotope dilution. Sample introduction was carried out with a PFA-100™ microflow nebulizer coupled to a cryogenic desolvation unit kept at -5 °C. Oxygen was introduced as auxiliary gas to avoid carbon deposits on cones and lenses. 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. The recoveries obtained were within the range of 85 % to 120 %, confirming the accuracy of the method. The RSDs were lower than 3 % for isotope dilution, and 11 % for external calibration, indicating precision of the applied methods. The concentrations, in mg kg-1, found for Ni and Cr in CAP by isotope dilution were, respectively, 40.7 ± 1.0 and 1.8 ± 0.04, while for external calibration the results were, respectively, 39.1 ± 2.2 and 1.6 ± 0.2. The methods demonstrated efficiency in the determination of Ni e 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.

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