ICP-MASS SPECTROMETRY

Analysis of Petroleum Samples by DRC-ICP-MS

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Introduction

The analysis of petroleum products (i.e. gasoline, oil, and diesel) presents a challenge for ICP-MS. Owing to the nature of these samples and their associated highly organic solvents, a number of analytical challenges are encountered.

First, the high degree of volatility of the samples increases the vapor loading and causes destabilization of the plasma. This is observed in the form of decreased precision as well as the intermittent shutdown of the plasma.

Second, these samples are rich in carbon, which is poorly ionized in the plasma due to its high first ionization potential (11.26 eV). As a result, non-ionized carbon deposits in its elemental form and clogs the interface cones. Also, the addition of oxygen to the plasma (to burn the excess carbon) can have the adverse effect of destabilizing the plasma by continuously changing its overall impedance.

Finally, the high levels of carbon lead to a number of carbon-based polyatomic interferences on several analytes of interest, such as those shown in Table 1.

Fortunately, these challenges can be overcome. The ELAN® ICP-MS family of instruments features a 40 MHz free-running RF generator. This generator utilizes electronic tuning to compensate for the small shift of RF frequency brought about by the impedance change in the plasma. Unlike 27 MHz fixed frequency generators, this compensation is virtually instantaneous because there are no moving parts. As a result, the ELAN offers a very robust plasma capable of remaining lit even when highly volatile samples are aspirated.

The use of a Peltier-cooled spray chamber reduces the amount of matrix vapors reaching the plasma. This means that the sample introduction system delivers a higher analyte/matrix ratio to the plasma.

Finally, the use of a Dynamic Reaction Cell™ (DRC™) offers a superior way to eliminate carbon-based polyatomic interferences without sacrificing analyte sensitivity. This is accomplished by introducing a highly reactive gas that reacts preferentially with the polyatomic ions but not with the ions of interest.

This work demonstrates the ability of the ELAN DRC II to analyze petroleum samples which have been diluted with kerosene.

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Table 1. Carbon-based Polyatomic Interferences.

Element	Interference
Mg^+	C_2^+
Al^+	CNH^+
Ca^+	CO_2^+
V^+	$^{38}Ar^{13}C^+$

Experimental

Instrument Parameters

All analyses were performed on an ELAN DRC II using ammonia as the reaction gas to remove polyatomic interferences. The instrument was equipped with the Peltier-cooled organic sample introduction system, a 0.85 mm injector and an oxygen mass flow controller. The nebulizer used was a PFA-ST (Elemental Scientific Inc., Omaha, NE USA) which was self aspirating at a sample uptake rate of 100 µL/min. The sample aerosol passed through a Peltier-cooled cyclonic spray chamber with an oxygen inlet port (PC-3, Elemental Scientific Inc., Omaha, NE USA). The spray chamber was chilled to -5 ˚C, and oxygen was introduced at 0.02 L/min. Upon exiting the spray chamber, the aerosol entered the 1550 W plasma. A picture of the sample introduction system appears in Figure 1.

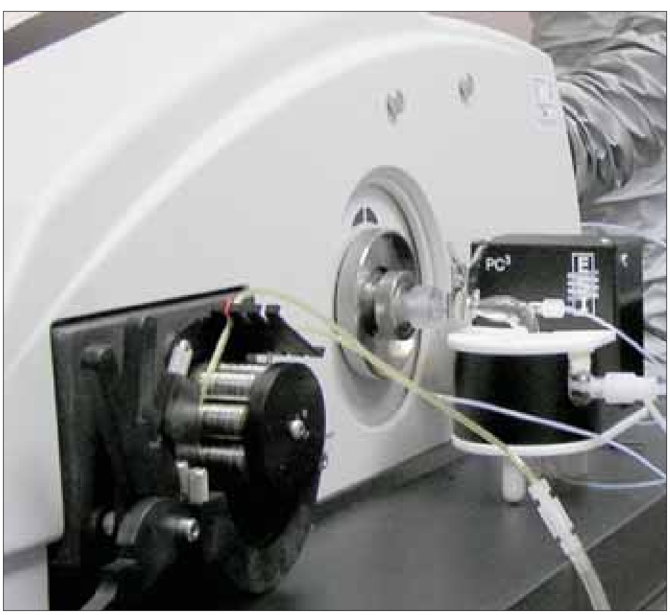

Figure 1. Photo of the sample introduction system used for the analysis of kerosene and petrol samples.

The elements of interest and their reaction cell conditions are listed in Table 2. Ammonia was used as a reaction gas. Where possible, multiple isotopes of the same element were analyzed to confirm the results.

Table 2. Analytes and Reaction Cell Parameters.

Element	m/z	NH_3 Flow (mL/min)	RPq
B	10, 11	0	0.25
Na	23	0	0.25
Al	27	0	0.25
Ti	47	0	0.25
V	51	0	0.25
Mn	55	0	0.25
Ni	58, 60	0	0.25
Cu	63, 65	0	0.25
Zn	64, 66	0	0.25
Mo	95, 97, 98	0	0.25
Cd	110, 111, 114	0	0.25
Sn	118, 120	0	0.25
Ba	135, 138	0	0.25
Pb	206, 208	0	0.25
Mg	24	0.5	0.5
Al	27	0.5	0.5
Ca	40	0.5	0.5
V	51	0.5	0.5
Cr	52, 53	0.5	0.5
Fe	56	0.5	0.5

Samples

Samples and calibration standards were supplied in a kerosene matrix and analyzed without further preparation. Yttrium and indium were used as internal standards.

Results

The calibration curves for magnesium and chromium are shown in Figure 2. The linearity of these curves indicates that the carbon interferences have been removed; if these interferences were not removed, the curves would not be linear. Typical results for one of the samples appear in Table 3, along with the Background Equivalent Concentrations (BECs). The uncertainty was determined from three consecutive analyses of the sample. For clarity, only one isotope for each element is shown.

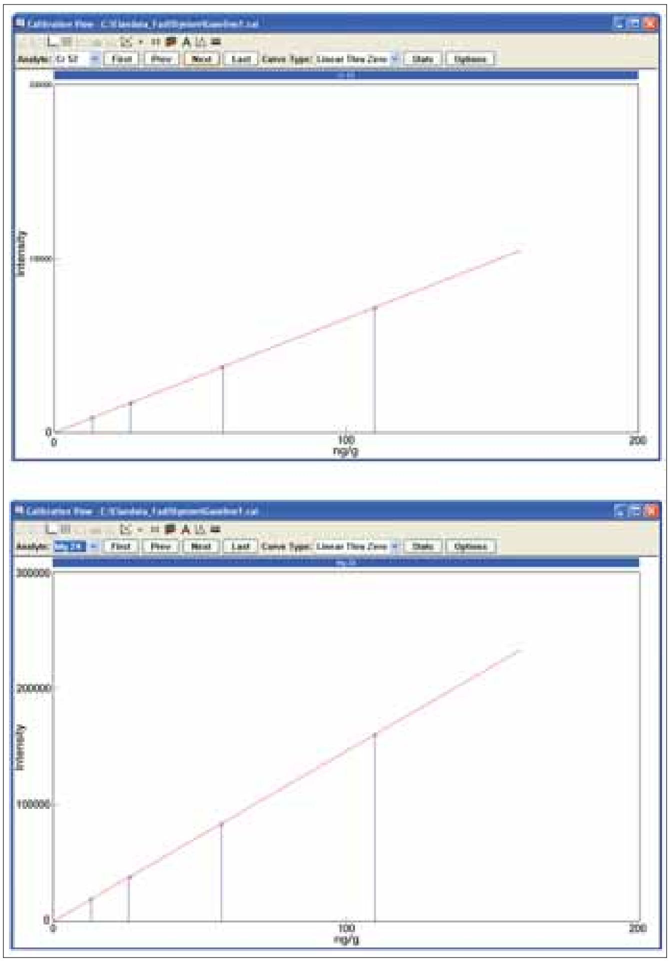

Figure 2. Calibration curves for chromium and magnesium in kerosene.

To confirm the results for calcium and iron, these elements were also analyzed under a second set of DRC conditions; the conditions and results are shown in Table 4. The results for Ca and Fe agree under both sets of DRC conditions, thus confirming that the answers are correct. The ability to analyze the same isotope under different reaction conditions highlights an additional advantage – confirmation of results by analyzing the same isotopes under multiple conditions.

These results demonstrate that low levels of the elements can be measured in petroleum samples in kerosene.

Table 3. BECs and Typical Results for the Samples.

Element	m/z	BEC	Sample
B	10	5.68	12.06 ± 0.33
Na	23	8.81	15.84 ± 0.35
Ti	47	2.73	15.51 ± 0.20
Mn	55	0.21	16.06 ± 0.06
Ni	60	0.36	15.81 ± 0.08
Cu	63	1.49	16.01 ± 0.10
Zn	66	4.23	14.98 ± 0.06
Mo	98	0.02	16.21 ± 0.10
Ag	109	0.08	16.11 ± 0.02
Cd	114	0.07	14.31 ± 0.04
Sn	120	0.46	16.36 ± 0.02
Ba	138	0.10	16.24 ± 0.02
Pb	208	0.65	16.26 ± 0.05
Mg	*24*	*0.35*	15.17 ± 0.08
Al	*27*	*0.27*	16.42 ± 0.33
Ca	*40*	*3.45*	16.31 ± 0.05
V	*51*	*0.01*	15.96 ± 0.08
Cr	*52*	*0.07*	16.14 ± 0.06
Fe	*56*	*1.14*	16.32 ± 0.18

*Results in italics were determined in DRC mode (all units are µg/kg).

Table 4. Determination of Ca and Fe with Alternate Conditions.

Analyte	m/z	NH_3 Flow (mL/min)	RPq	Sample (µg/kg)
Ca	40	0.9	0.5	16.19 ± 0.24
Fe	56	0.9	0.5	16.04 ± 0.02

Conclusion

This work has shown the ability of the ELAN DRC II to measure low analyte levels in petroleum samples dissolved in kerosene. The DRC removed the effects of carbon interferences, while the unique RF generator, in combination with a chilled spray chamber and low uptake nebulizer, allowed samples to be run without clogging cones or the injector and without extinguishing the plasma.

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