

# Direct Determination of Trace Metal Impurities in Petroleum and Oil Products using ICP-MS

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## Overview

**Purpose:** To develop a simple, direct, rapid and accurate method for the quantification of metallic impurities in naphtha, vacuum gas oil (VGO) and aviation turbine fuel (ATF) by ICP-MS.

**Methods:** Samples were simply diluted in kerosene and analyzed directly by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) equipped with collision/reaction cell technology for interference removal.

**Results:** All 3 samples investigated were successfully analyzed for 14 elements at trace levels. Sub-ppb limits of detection (LODs) were achieved for all analytes.

## Introduction

Metallic impurities such as nickel, vanadium, and sulphur, are known to be catalyst poisons in the petroleum industry, even when they are present at only trace levels. Premature failures of catalysts can easily cost millions of dollars and hence monitoring of these elements is extremely important. Additionally, costs associated with maintenance due to engine and machine wear can be significant. Determination of additive elements, wear metals and contaminants in unused and used lubricating oils is therefore helpful. ASTM methods based on ICP-OES are available for used and unused lubricating oils<sup>1,2</sup> with detection limits in the mg/kg (ppm) range for most of the elements. However, requirements are becoming stricter and in an effort to improve detection limits down to the sub µg/kg (ppb) range, a method was developed using the Thermo Scientific™ iCAP™ Q ICP-MS.

Analysis of combustible organic samples such as naphtha, VGO, and ATF with ICP-MS is a challenge, because of the high volatility of the sample (which can cause unexpected and intermittent extinguishing of the plasma), carbon deposition and carbon based interferences<sup>3</sup>. As these samples are not soluble in water, they cannot be analyzed by conventional aqueous methods. They must therefore either be converted to a water soluble form, by labour intensive and time consuming microwave digestion, or a method for direct analysis of the organic sample must be developed.

This poster outlines the development of a method that enables direct analysis of these samples with ICP-MS. A special introduction system, combined with oxygen addition to the plasma, was used to compensate for the increased vapour load and presence of carbon that result from analysing these organic samples directly.

## Methods

### Sample Preparation

Calibration standard solutions were prepared using certified reference standards (Conostan®, SCP SCIENCE, Canada) by appropriate dilution with white kerosene in the range 1 to 50 µg/kg. VGO was diluted 50-fold with kerosene and naphtha and ATF were undiluted. Samples were then introduced without further preparation into the ICP-MS for analysis.

### Test method

All samples were analyzed using the iCAP Qc ICP-MS (Figure 1) equipped with an organics kit (i.e. a PFA-µFlow nebulizer, quartz cyclonic spray chamber, Peltier-cooled to -15°C, 1.5 mm ID quartz injector) and additional mass flow controller for the introduction of oxygen to the plasma at 78 mL/min. The iCAP Qc ICP-MS was operated in STD mode for non-interfered analytes and KED mode with pure helium as the cell gas for interfered analytes.

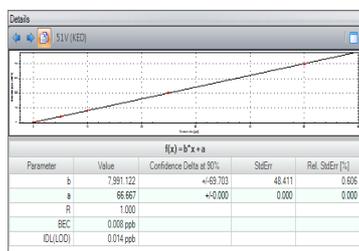
### Data Analysis

Qtegra ISDS software was used for collection and processing of all data from the iCAP Qc ICP-MS. Calibration was performed using an external calibration within the Qtegra ISDS software. As an example, the calibration obtained for vanadium in KED mode is presented in Figure 2.

FIGURE 1. The Thermo Scientific iCAP Q ICP-MS



FIGURE 2. Vanadium calibration in kerosene



## Results

Advanced collision cell technology operation with the iCAP Qc ICP-MS QCell, run in kinetic energy discrimination (KED) mode, was used for minimising polyatomic interferences for many of the metals. For non-interfered analytes, standard (STD) mode was used, with in-sample mode switching applied so that all the analytes could be measured in a single run. Table 1 shows a summarized list of the analytes with their measurement mode, sensitivity and limit of detection.

TABLE 1. Measurement mode, sensitivity and limit of detection data.

Analyte	Mode	Mass (m/z)	Sensitivity (cps/ppb)	R value	LOD (ng/ml)
Molybdenum (Mo)	STD	95	20211.9	1.000	0.131
Nickel (Ni)	KED	60	6798.5	1.000	0.121
Potassium (K)	KED	39	578.9	1.000	0.607
Silver (Ag)	STD	107	105839.2	1.000	0.001
Sodium (Na)	STD	23	157486	0.996	0.741
Arsenic (As)	KED	75	711.6	1.000	0.126
Mercury (Hg)	STD	202	7285.7	1.000	0.030
Magnesium (Mg)	KED	24	741.7	1.000	0.269
Cadmium (Cd)	STD	111	12154.9	1.000	0.006
Chromium (Cr)	KED	52	14482.7	1.000	0.015
Copper (Cu)	KED	63	24697.0	1.000	0.067
Lead (Pb)	STD	208	200124.3	0.999	0.125
Manganese (Mn)	STD	55	176758.6	1.000	0.063
Vanadium (V)	KED	51	7991.1	1.000	0.014

The analysis results (in ng/mL) for the 3 sample types are shown in Table 2.

TABLE 2. Concentrations of trace elements in naphtha, ATF and VGO

Element	ATF	Naphtha	VGO
Molybdenum (Mo)	< 0.1	< 0.1	< 5.0
Nickel (Ni)	< 0.1	< 0.1	29.3
Potassium (K)	< 0.1	< 0.1	< 5.0
Silver (Ag)	< 0.1	0.50	< 5.0
Sodium (Na)	1.94	< 0.1	57.35
Arsenic (As)	< 0.1	0.53	257.5
Mercury (Hg)	< 0.1	0.91	< 5.0
Magnesium (Mg)	1.32	< 0.1	< 5.0
Cadmium (Cd)	< 0.1	< 0.1	< 5.0
Chromium (Cr)	< 0.1	0.13	< 5.0
Copper (Cu)	0.25	0.9	< 5.0
Iron (Fe)	< 0.1	< 0.1	192.3
Lead (Pb)	< 0.1	< 0.1	12.4
Manganese (Mn)	< 0.1	< 0.1	< 5.0
Vanadium (V)	< 0.1	< 0.1	< 5.0

- The performance of the free running RF generator of the iCAP Qc ICP-MS for successfully tolerating volatile organic samples
- Rapid, simple and accurate analysis of petrochemical samples, using direct sample introduction after dilution with kerosene, where required.
- Robust analysis even with challenging samples such as volatile naphtha, viscous VGO and ATF

## References

1. ASTM D 4628
2. ASTM D 5185
3. EPA METHOD 6020A

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