application note

Determination of Various Elements in Highly Volatile Organic Matrices (Naphtha)

Introduction

Light naphtha (boiling point range 40–150 degrees Celsius) is used as a fuel for gas turbines. The cost of maintenance due to engine and machine wear can be significant and therefore high importance is placed on a diagnostic method for monitoring equipment status. The determination of trace impurities in highly volatile matrices such as petrol and naphtha has been described by various analytical techniques such as Volumetric analysis, Titrimetry, Colorimetry, Atomic Absorption (AAS) and X-Ray Fluorescence spectrometry (XRF).

More recently though, a great deal of interest has been shown in Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). Its multi-element capabilities, minimal sample preparation involved, high sensitivities and large linear dynamic range offer a highly productive and attractive alternative. However, researches have had to refine the ICP technique to overcome problems such as carbon build up and quenching of the plasma due to the high solvent loadings typically associated with the analysis of highly volatile, low boiling point, organic matrices.

In the past, carbon build up was reduced by the addition of oxygen to the plasma to ensure an oxidising environment. However, this added to the complexity of the instrumentation. The high solvent loadings into the plasma were reduced by dilution of the low boiling point matrix with high boiling solvents such as kerosene and xylene. Whilst this proved to be a fairly simple approach to the solvent loading problem, it did result in an extra time consuming step in the sample preparation procedure as well as a dilution of the detectable levels resulting from the typically 5 to 10 fold dilutions.

This paper compares two different approaches to the analysis of highly volatile matrices such as petrol and naphtha by ICP. One approach makes use of a jacketed spraychamber with temperature cooling whilst the second approach utilises an ultrasonic nebulizer with desolvator. Both approaches eliminate the time consuming dilution step of traditional ICP methods. Neither approach requires the addition of an extra gas, oxygen, into the plasma stream to minimize carbon build up. Both approaches utilize all the ICP advantages previously highlighted in this report with the only differences between the two techniques being the sensitivity and initial costs.

Experimental

Standard Preparation

A 1 ppm multi-element standard containing Ag, Ba, Al, P, B, Ca, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, Pb, Si, Sn, Ti, V and Zn was prepared by accurately weighing 1.000 g of a 100 ppm Conostan S-21 standard in hydrocarbon oil into a 100 mL volumetric flask and making to volume with unleaded petrol. A similar standard was prepared by making up to volume with naphtha provided by Mobil Australia. The standards were also spiked with 1 ppm of Hg and As by adding 1.000 g of a 100 ppm Hg and a 100 ppm As standard into the volumetric flasks.

Integra Operating Parameters

As Integra provides computer control of over 200 instrument parameters, operating parameters optimized for the individual applications can readily be determined and stored in method files to be recalled at any time for analysis. Integra's unique and sophisticated auto-optimisation software was used to optimize the operating parameters for the critical toxic elements Pb and Cd.

The optimised parameters were:

Viewing Height Individually Optimised	9 mm
Nebulizer Gas Flow Optimised for Cd/Pb	0.65 L/min (160 kPa)
Power	1200 W
Plasma Gas Flow	12 L/min
Auxiliary Gas Flow	0.7 L/min
Sample Uptake Rate	1.2 mL/min
PMT Voltage	600 V

Measurement Conditions ;

Integration Time	10 s
Replicates	11
Background Correction	Fixed Point
Scan Windows	0.08 nm 1st Order 0.04 nm 2nd Order 0.027 nm 3rd Order 0.02 nm 4th Order

Principle of the Jacketed Spraychamber

The jacketed spraychamber is similar to the normal glass cyclonic spraychamber, but with a surrounding glass envelope. Coolants such as ethylene glycol can be circulated through the inner wall between the glass envelope and spraychamber through the two connections from a water bath. When cooled to approximately 0^{o}C, the rate of nebulization is reduced ensuring that when highly volatile organics such as petrol or naphtha are aspirated, the solvent loading to the plasma is sufficiently reduced to allow direct aspiration of the most difficult, highly volatile organic matrices.

***Figure 1**. Jacketed Spraychamber*

This eliminates the time consuming dilution step with less volatile organics such as kerosene and xylene of traditional ICP-OES methods and improves the detection limits for the method as trace impurities are no longer diluted.

Principle of the Ultrasonic Nebuliser with Membrane

The sample is pumped to a transducer plate which vibrates at high frequencies of about 1.5 kHz. This results in a very dense aerosol that is then carried through a heating and condensing stage to remove as much of the solvent as possible, allowing mostly the dry vapour containing the analytes to be carried through to the plasma. With highly volatile solvents such as petrol and naphtha, a secondary desolvation stage is required due to the higher generation of small droplets compared to aqueous solutions. This is performed by the membrane.
Effectively, the ultrasonic nebulizer is a pre-concentration device that also aids in removing a significant proportion of the solvent to allow direct aspiration of highly volatile matrices with the added advantage of 5 to 20 times improvements in detection limits.

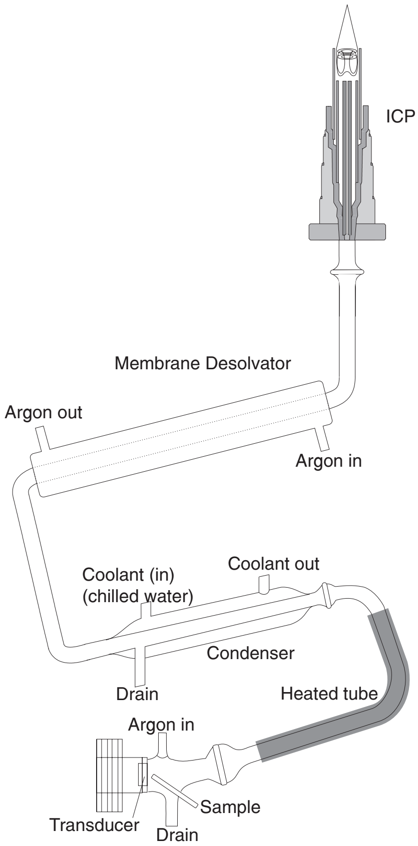

***Figure 2**. Ultrasonic Nebulizer with membrane*

Typical operating conditions are:

Desolvation Temperature	140°C
Cooling Temperature (Peltier)	-10°C
Sample Delivery	1.5 L/min
Aerosol Carrier	0.3-0.7 L/min
(Optimised Individually per element)	
Heating Tube Temperature	160°C
Sweep Gas	0.2 L/min

Setup is rapid, taking less than one minute to interchange from Integra's standard set of sample introduction components and operation is simplified with automatic temperature control of the heating and cooling functions. The compact design allows convenient placement of the ultrasonic nebulizer on Integra's standard built in bench, ensuring optimum use of laboratory space.

Results

Table 1 shows the wavelengths selected and their corresponding measured detection limit. The detection limit reported is based on three standard deviations of the blank using 11 replicates of 10 s integration.

Element	(nm)	Jacketed (ppb)	USN (ppb)	Improve Factor
Ag	328	3	1	3
Al	167	3	0.5	6
S	188	40	12	3
B	249	1.5	0.7	2
Ba	455	1.5	0.2	8
Ca	393	0.1	0.06	2
Cd	214	1	0.2	5
Cr	283	3	0.4	8
Cu	324	3	0.5	6
Fe	259	3	0.3	10
Hg	184	10	9	1
Mg	279	0.1	0.02	5
Mn	257	0.6	0.1	6
Mo	202	12	1	12
Ni	221	4	1	4
P	177	12	1	12
Pb	220	30	2	15
Se	196	50	15	3.5
Si	251	6	1	6
Sn	189	27	5	5
Ti	334	4	0.3	13
V	309	11	1	11
Zn	213	2	0.3	7

Table 1: Detection Limits for Naphtha (3 sigma)

Conclusion

Two techniques have been presented that allow the multi-element and productivity advantages of ICP-OES to be utilized for specialized petrochemical applications such as the determination of trace impurities in naphtha. Both techniques may also be applied to petrol (gasoline) samples. Neither technique requires the addition of oxygen to the plasma to eliminate carbon build up. These techniques allow direct aspiration of highly volatile organic matrices, eliminating time consuming dilution steps of traditional ICP-OES methods. Subsequently, both techniques offer improved detection limits on the traditional ICP methods, with the method of ultrasonic nebulization offering 2 to 20 fold improvements over the jacketed spraychamber technique, depending on the eluent.

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