

# An investigation in to the use of sample introduction accessories to improve organic analysis on ICP

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## Abstract

Analysis of organic solvents by ICP is often seen as problematic and challenging due to the nature of the solvents used. Commonly encountered problems include structured background in the visible region resulting from molecular carbon based emissions, high plasma loading and the possibility of carbon depositions. The high volatility of the solvents results in high plasma loading when compared to aqueous solvents. Traditional ICP's employ the use of RF generators that contain complex matching networks that are slow to respond to changes in plasma loading. This is no longer the case, as with latest generation of ICP's such as the iCAP 6000 series from Thermo Fisher Scientific which use swing frequency RF generators which are extremely quick to respond to any change in plasma loading making the analysis of organic solvents a simple everyday process.

The analysis of complex organics can be further simplified by the use of accessories to remove the solvent prior to sample being introduced in to the plasma. The removal of the solvent has two benefits firstly reducing the plasma loading and secondly by simplifying the spectrum produced by the sample by removing the molecular carbon emissions. The addition of oxygen to the plasma can also help in the second of these two. This paper sets out to look at the effectiveness of a number of these accessories to determine their usefulness in every day analysis of complex organic matrices when used with an iCAP 6000 ICP from Thermo Fisher Scientific.

## Introduction

The analysis of metallic elements in organic solvent is now common place in many laboratories. The main application is the analysis of new and used lubrication oils for additives elements and wear metals. Another major area is the analysis of trace elements in refinery based associated products such as crude oils, and a variety of distillates. A number of prescriptive methods such as those produced by ASTM and DIN committees exist for this type of analysis but in general they were developed a number of years ago and are only reviewed periodically, with little change and generally do not take into account any major advancements in analytical technologies.

One area where these methods are very non prescriptive is with regards to the sample introduction systems used on analytical instruments. This means that many laboratories can take advantage of advancements in sample introduction systems without deviating from the prescribed methods, improving the ease of analysis, sample through put as well as the precision and accuracy of the method.

FIGURE 1. The APS 1650 Auto-diluter The Thermo Scientific iCAP 6500



## Auto-samplers

### Samples

The first step in any reproducible analysis is the sample preparation, for oils this is relatively simple with a dilution (normally by a factor of ten). The vast majority of the prescriptive methods call for this to be carried out on a weight basis, this to correct for any differences in density/viscosity between samples. Dilutions carried out by weight are time consuming and also carry the added potential for human error. A simpler option would be to dilute by volume. The APS 1650 autodiluter (Figure 1) with organic solvent capabilities (CETAC Technologies, Omaha, NE, USA) was used to dilute the samples. The APS 1650 dilutes on a volume basis, and it was investigated if the results obtained by diluting a sample on a weight basis were comparable to those obtained when diluting on a volume basis. Both un-used and used oil were analyzed. The volumes of the dilution were set after taking into account the average density of the samples (0.7g/ml) and the solvent. This solvent contained an internal standard to correct for any small differences in viscosity between samples. Both of the solutions diluted manually by weight and automatically by volume were analyzed on the iCAP 6500 radial ICP from Thermo Fisher Scientific

### Method

Used oil samples subject for analysis of wear metals contain particulate matter, which can often lead to un-reproducible analysis. Autosamplers have now been developed to deal with this problem. Prior to analysis the sample is automatically homogenized by the auto-sampler. One such auto-sampler is the ASX 1400 (CETAC Technologies) Figure 1. Both new and used oil samples were diluted (twenty replicates of each) with the APS 1650 auto-diluter, homogenized and left prior to analysis for a period of one hour before analysis. Half of the replicates of each sample were re-homogenized immediately prior to analysis and half were not.

Chart 1. The spread of replicates of old oil (with particulate matter) and new oil (no particulate matter) without and with re-homogenization prior to analysis of Iron.

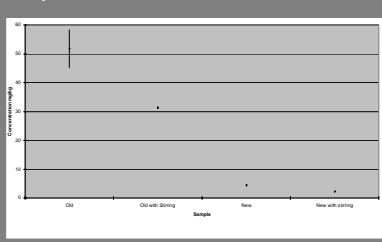


Figure 2. Details of the ASX1400 homogenization unit.



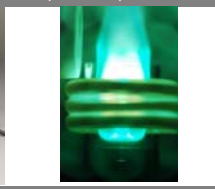
## Results

The un-homogenized replicates of the used oil samples that contained particulate matter show a large spread in the results with the RSD between samples as large as 10% in some cases. When the samples were re-homogenized, the replicates were analyzed again and the RSDs decreased by a factor of ten for samples containing particulate matter. The concentration of elements in the re-homogenized samples were found to be lower than in the un-homogenized samples. This is because in the un-homogenized sample, the particulates have migrated to the bottom of the auto-sampler tubes which is where the auto-sampler probe samples from, and thus preferentially sampling the particulate metals. In the new oil samples, which contained no or very little particulate matter, the process of re-homogenization made very little difference.

Figure 3. The IsoMist from Glass Expansion



Figure 4. An organic plasma show the correct position of the plasma



## Spray chambers

### Method

The analysis of organic solvents by ICP is often seen as problematic, even more so when the solvents are volatile. A volatile solvent (with respect to ICP) is defined as a solvent which exhibits a vapour pressure of greater than 30mm Hg. When a volatile solvent such as naphtha is introduced into an ICP, the sample transportation efficiency is much greater than that with aqueous samples and this leads to undesirable effects such as plasma instability and in some cases the plasma will be extinguished.

To introduce a solvent such as naphtha into a plasma the volatility must first be reduced; this can be done in two ways either by dilution with another solvent such as kerosene or by cooling the solvent prior to introduction into the plasma this is typically done with a cooled spray chamber. The second of these two options is preferable as this first will degrade the sensitivity of the analysis.

The iCAP 6500 Radial ICP was used for this analysis. The radial was chosen as the interferences from carbon based emissions can be reduced by optimising the radial viewing height. The IsoMist from Glass Expansion, Figure 3) a programmable temperature controlled spray chamber was used in conjunction with a glass concentric nebuliser for this analysis.

Standards were prepared by diluting Conostan S21 300mg/kg oil based standard in naphtha (Fisher Scientific) to 1.1 and 4.8 mg/kg, a blank was prepared from the naphtha. A blank naphtha sample was also spiked to 2.4mg/kg using the Conostan S21 standard.

The IsoMist was set to -5° C. Naphtha was then aspirated in to the IsoMist and the plasma was observed. The auxiliary gas flow was adjusted until the base of the plasma was half way between the top of the auxiliary tube and the base of the load coil. The nebuliser gas flow was adjusted until the green sample channel was just below the top of the torch (Figure 4). The radial viewing height was adjusted using the optimize source function of iTEVA to give the best signal to background ratio for all of the elements to be analysed.

The instrument was then calibrated and the spiked sample analysed. A detection limit was carried out by analysing the calibration blank with 10 replicates and multiplying the standard deviation of this analysis by 3. The subarray plots for each of the wavelengths were examined to ensure that they were interference free and the correct background correction points were used.

Results	Naphtha spike at 2.4mg/kg		RSD on three replicates of the spike	Instrument Detection Limit
	mg/kg	%		
Ag 338.369 nm	2.39	0.558	0.8	
Al 308.215 nm	2.37	0.188	2.6	
B 208.890 nm	2.17	1.207	3.8	
Ba 223.827 nm	2.35	0.637	1.3	
Ca 184.006 nm	2.35	1.426	8.1	
Ca 214.438 nm	2.38	0.970	1	
Co 267.716 nm	2.37	0.246	0.8	
Co 324.754 nm	2.41	0.207	0.4	
Fe 238.204 nm	2.39	0.546	1.8	
Mg 279.553 nm	2.40	0.087	0.08	
Mn 293.939 nm	2.38	0.227	0.8	
Mo 281.035 nm	2.38	0.215	2.2	
Ni 589.992 nm	2.41	0.546	1.9	
Ni 231.064 nm	2.37	0.751	5.0	
P 178.284 nm	2.40	0.442	15	
Pb 283.553 nm	2.35	0.391	16	
Se 212.412 nm	2.40	0.467	10.5	
Sn 283.999 nm	2.37	0.456	20	
Ti 334.941 nm	2.37	0.153	0.4	
V 309.311 nm	2.37	0.387	0.9	
Zn 213.856 nm	2.39	0.235	0.8	

## Conclusions

The analysis of organic solvents for trace metals can be simplified by enhancing the sample preparation and the sample introduction. The automation of the dilution process removes human error as well as speeding the process up. The addition of a stirring auto-sampler allows samples which contain particulate matter to be homogenised immediately prior to analysis improving both repeatability and accuracy. The analysis of volatile solvents such as naphtha on the iCAP is made possible by the addition of a temperature controlled sprayed chamber set to -5° C. This reduces the volatility of the solvent which in turn will lower the plasma loading when the solvent is aspirated. The Thermo Scientific iCAP 6000 Series is capable of detecting single figure and sub ppb amounts within this matrix.