

# SPECTRO

# REPORT

APPLICATION REPORT 76  
SPECTROFLAME ICP

## THE DETERMINATION OF TRACE IMPURITIES IN ORGANIC SOLVENTS

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### ABSTRACT

It has been demonstrated that trace impurities in undiluted ethanol, isopropanol, xylol and kerosene can be determined with the SPECTROFLAME ICP with excellent plasma stability. Because the physical properties of organic solvents often differ greatly from those of aqueous solutions, the process of generating the aerosol also differs frequently when compared with the process for aqueous solutions. Thus, it may be necessary to newly optimize the instrumental operation parameters for organic solvents with respect to analytical figures of merit. New optimization of the plasma long-term stability may also be required. This is especially true for ethanol and isopropanol, for which a minimum generator power of 1400 W should be used. Kerosene and xylol can be analyzed with the same ICP operating conditions used for the analysis of aqueous solutions.

### 1. INTRODUCTION

The majority of the analyses conducted with ICP spectrometry are performed for inorganic, aqueous solutions; for example of polluted or non-polluted waters, metals, steel or geological samples.

If the elements to be determined are present in an organic matrix for example food or vegetable samples, the matrix is often removed by ashing or digestion prior to analysis. Inconvenient ashing or digestion processes could be avoided by the direct determination of elements in organic solvents.

Extraction with an organic solvent for preconcentration is still required for other samples. Determination of the elements then follows in the organic matrix; e.g., to improve the detection limits or for speciation analysis.

The direct determination of impurities in organic solvents is also frequently of interest; in the oil or fat processing industries, for example. Thus, the direct analysis of organic samples or solvents with ICP spectrometry becomes necessary.

In contrast to aqueous solutions, there may be significant differences for aerosol generation as well as in the excitation conditions for the elements in the plasma for organic solvents [1, 2].

A distinct green coloration in the aerosol channel, due to emission from C bands, is visible with the naked eye when an organic solution is nebulized. It is always important to exercise great care when selecting the spectral lines for the analysis; it is necessary to check for spectral interferences due to C, CO and CH bands. Compared to water, there are differences in the aerosol efficiency and in the drop-size distribution when nebulizing organic solvents. These differences are due to variations in the density, surface tension, viscosity and vapor pressure of the solutions. The above mentioned differences from aqueous samples often make it necessary to adjust the ICP operating conditions. The required adjustments are discussed in this report. In addition, the analytical figures of merit are compared for several elements in various organic solvents.

## 2. INSTRUMENT DESCRIPTION AND OPERATION PARAMETERS

There are four SPECTROFLAME ICP models: SPECTROFLAME COMPACT S, SPECTROFLAME COMPACT E as well as SPECTROFLAME MODULA S and SPECTROFLAME MODULA E. The former two instruments are benchtop instruments with three optical systems (two polychromators and one monochromator); they are available with radial plasma observation (side-on) as the COMPACT S or with axial plasma observation (end-on) as the COMPACT E. The highest quality, speed and flexibility are ensured by the selection of 43 simultaneous channels combined together with a monochromator.

Up to five optical systems can be included in the SPECTROFLAME MODULA S (side-on observation) and E (end-on observation) instruments which are available as stand-alone or benchtop models. These instruments can be equipped with a UV spectrometer and up to two monochromators and three polychromators; allowing highest flexibility in line selection.

The best possible light transmission in the UV/VUV region is ensured at all times, as all of the optical systems for the UV/VUV region are built into a vacuum-proof tank that is filled with highly pure nitrogen. The optical components are protected from all contamination by this system.

All of the measurements for this application were conducted with a SPECTROFLAME MODULA S (side-on observation) equipped as described in Tables 1 and 2. The instrumental operation parameters are listed in Table 3, if not given in the text.

Table 1: Instrument description

Generator:	free-running, 27.12 MHz
Sample introduction:	
Peristaltic pump:	12 rollers
Nebulizer:	cross flow (SPECTRO)
Spray chamber:	according to Scott (SPECTRO)

Table 2: Optical system

Optic	Wavelength Range (nm)	Grating (lines/mm)	Fill Medium
UV-mono-chromator	160 to 460	2400	nitrogen
2 poly-chromators	210 to 460	3600	air
1 Poly-chromator	324 to 853	1800	air



Table 3: ICP operating parameters for various solvents

Parameter	Water		Kerosene and Xylol		Ethanol and Isopropanol	
Power	1200	W	1200	W	1400	W
Pump rate	2	mL/min	2	mL/min	0.6	mL/min
Observation height	15	mm	15	mm	15	mm
Nebulizer gas pressure	3.2	bar	3.2	bar	3.2	bar
Nebulizer gas flow rate	1	L/min	1	L/min	1	L/min
Auxiliary gas flow rate	1	L/min	2	L/min	2	L/min
Coolant gas flow rate	12	L/min	12	L/min	16	L/min

### 3. RESULTS AND DISCUSSION

The physical properties for the solvents examined in this report are displayed in Table 4. Compared to water, the organic solvents have a lower density and lower surface tension. Ethanol and isopropanol have lower boiling points and higher vapor pressures than water. The physical properties described here for the samples have a decisive influence on generation of the aerosol. Therefore, the instrumental operation parameters for the SPECTROFLAME ICP were optimized for organic solvents. The optimized instrumental parameters are listed for each of the solvents in Table 3. It is possible to work with the same parameters for the analysis of xylol and kerosene as for the analysis of aqueous solutions. However, it is advantageous to use a somewhat higher auxiliary gas flow rate (2-3 L/min instead of 1 L/min) in order to avoid carbon deposits on the injection tube. If these sooty deposits do occur, they can be easily blown away with a dry gas current from the torch's quartz glass tube. A higher power together with a higher coolant gas flow rate are advantageous for the analysis of ethanol (EtOH) and isopropanol (IPA) in order to avoid extinguishing of the plasma (see also Table 3, Figure 1). Beginning with 1400 W, the plasma is very stable, even without utilizing special precautions; e.g., the use of a cooled spray chamber. The heating in the sample introduction chamber should be turned off and the pump rate reduced when analyzing organic solutions. A pump rate of 0.6 mL/min (see Table 3) should be used for the analysis of ethanol and isopropanol, in order to prevent extinguishing of the plasma.

Table 4: Physical properties for several solvents for normal conditions [3]

Solvent	Density (g/cm <sup>3</sup> )	Surface Tension (dyn cm <sup>-1</sup> )	Viscosity (cP)	Boiling Point (°C)
Ethanol	0.789	24.05	1.2	78
Isopropanol	0.785	23.78	0.78	82
Xylol	0.880	28.9	0.69	144
Kerosene	0.8	21.9	0.59	180
Water	0.998	72.8	1	100

The influence of the generator power (1000-1600 W) on the BEC for Cd is displayed for various solvents in Figure 1. The optimal BEC for Cd (Cd II 226.502 nm) in aqueous solution, kerosene or xylol lies in the range of power from 1200-1300 W.

With increasing power, the BEC for Cd increases for all of the solvents used (Figure 1). This is also true for most of the other elements listed in Table 5. The influence of the Nebulizer gas on the BEC for Cd (Cd II 226.502 nm) is displayed in Figure 2. The optimal Nebulizer gas flow rate lies between 0.9 and 1 L/min for all of the solvents. The nebulizer gas flow rate for obtaining the best BEC values did not differ significantly between organic and aqueous matrices. This trend was confirmed for the other elements listed in Table 5.

The detection limits ( $3\sigma$ ) determined for several elements in the solvents examined here are listed in Tables 5 and 6.



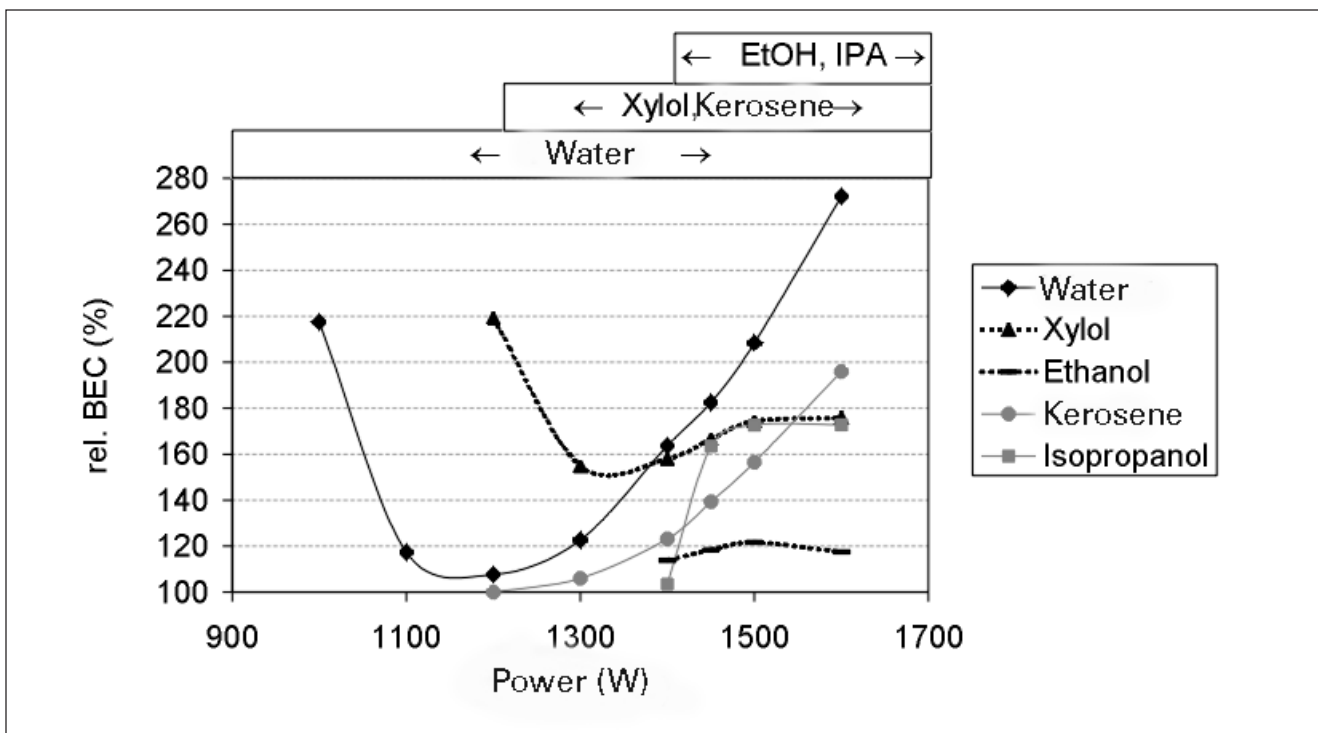


Figure 1: Optimal generator power range for several solvents and relative BEC's for Cd (Cd II 226.502 nm) in these solvents depending on the generator power (concentration, Cd: 2 mg/L, pump rate: 0.6 mL/min, coolant gas flow rate: 16 L/min, auxiliary gas flow rate: 2 L/min, nebulizer gas flow rate: 1 L/min)

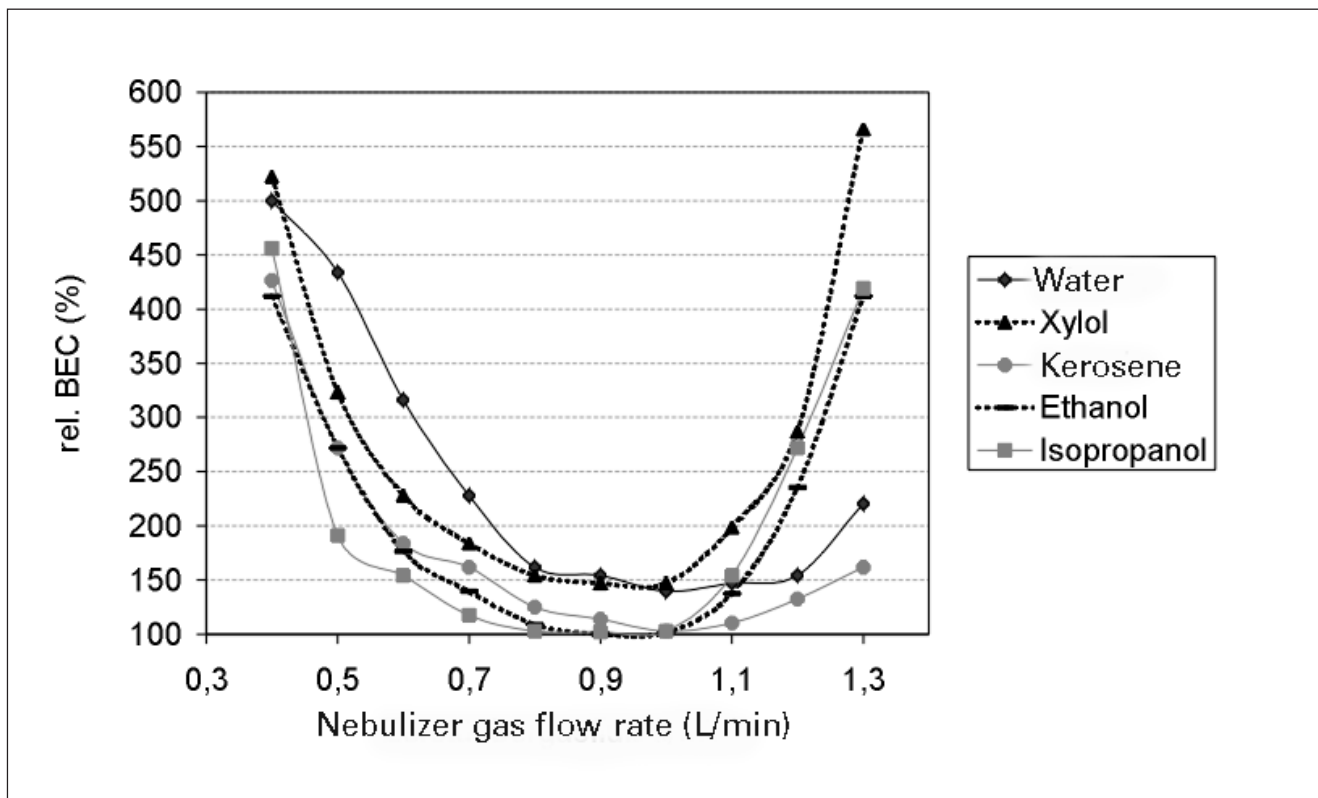


Figure 2: Relative BEC's for Cd (Cd II 226,502 nm) in various solvents depending on the nebulizer gas flow rate (concentration, Cd: 2 mg/L, pump rate: 0.6 mL/min, coolant gas flow rate: 16 L/min, auxiliary gas flow rate: 2 L/min, generator power: 1400 W)

Table 5: Detection limits (DL) in xylol and kerosene (see Table 3 for the instrumental parameters))

Element	Line (nm)	DL (Kerosene) (µg/kg)	DL (Xylol) (µg/kg)
Al	I 308.315	15.2	12.5
B	I 249.678	1.8	2.3
Ba	II 455.403	0.2	0.2
Ca	II 317.933	1.7	1.2
Cd	II 226.502	1.2	1.6
Cr	II 267.716	1.3	1.1
Cu	I 324.754	1.7	0.8
Fe	II 259.940	1.0	0.8
Mg	II 279.079	14.1	14.0
Mn	II 257.610	0.3	0.2
Mo	II 281.615	2.8	1.9
Na	I 589.592	11.7	5.4
Ni	II 231.604	4.2	4.5
P	I 177.500	3.0	3.2
Pb	II 220.353	16.6	21.4
Si	II 251.611	1.2	0.8
Sn	II 189.926	10.7	13.5
Ti	II 334.941	0.2	0.2
V	II 311.071	1.7	1.3
Zn	II 213.856	1.5	1.7

Table 6: Detection limits (DL) in ethanol and isopropanol (see Table 3 for the instrumental parameters))

Element	Line (nm)	DL (Ethanol) (µg/kg)	DL (Isopropanol) (µg/kg)
Al	I 308.315	6.2	19.3
B	I 249.678	1.4	1.9
Ba	II 455.403	4.0	4.0
Ca	II 317.933	3.2	11.0
Cd	II 226.502	2.3	2.9
Cr	II 267.716	1.3	4.3
Cu	I 324.754	2.5	3.3
Fe	II 259.940	1.1	0.6
Mg	II 279.079	36.8	21.6
Mn	II 257.610	0.2	0.2
Mo	II 281.615	5.2	7.4
Na	I 589.592	18.0	14.5
Ni	II 231.604	7.7	6.2
P	I 177.500	10.5	28.8
Pb	II 220.353	47.1	69
Si	II 251.611	3.5	4.0
Sn	II 189.926	6.6	20.6
Ti	II 334.941	0.5	3.5
V	II 311.071	1.4	5.1
Zn	II 213.856	6.0	5.2

#### 4. CONCLUSION

Undiluted solutions of xylol, kerosene, ethanol and isopropanol can be analyzed with excellent plasma stability with the SPECTROFLAME ICP without having to work with special precautions for sample introduction; e.g., cooling the spray chamber. In some cases, it is necessary to change the instrumental parameters for these solvents, due to the different physical properties of organic solvents in comparison with water. The analysis of ethanol and isopropanol requires a higher generator power (at least 1400 W) together with a higher coolant gas flow rate (16 L/min). The ICP operating conditions for the analysis of xylol and kerosene are comparable with those for aqueous samples. Thus, except for increasing the auxiliary gas flow rate, it is not necessary to apply additional requirement for the analysis of oils (e.g., waste oils, lubricating oils), which are typically diluted with kerosene for sample preparation.

#### 5. References

- [1] M. W. Blades, B. L. Caughlin, Excitation temperature and electron density in the inductively coupled plasma aqueous vs organic solvent introduction, *Spectrochim. Acta* 40B, 579, 1985
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- [3] R. C. Weast, M. J. Astle, W. H. Beyer, *Handbook of Chemistry and Physics*, 67th Edition, CRC Press, Boca Raton, Florida, 1985





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