Analysis of Incineration Solvents

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1 Introduction

Before solvent incineration, it is necessary to know the level of toxic metals, such as Hg, Cd, Pb, etc. In this application note, we will demonstrate that ICP-OES can be an easy technique to perform solvent analysis, provided that you have a robust plasma.

2 Principle

2.1 Technique used

The elemental analysis of solutions was undertaken by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The sample is nebulized then transferred to an argon plasma. It is decomposed, atomized and ionized whereby the atoms and ions are excited. We measure the intensity of the light emitted when the atoms or ions return to lower levels of energy. Each element emits light at characteristic wavelengths and these lines can be used for quantitative analysis after a calibration.

2.2 Wavelength choice

The choice of the wavelength in a given matrix can be made using the “profile” function, or by using Win-IMAGE, which is rapid semi-quantitative analysis mode using multiple wavelengths. The principle is the same in either case: record the scans of analytes at low concentration, and of the matrix. By superimposing the spectra, we see possible interferences.

3 Instrument specification

The work was done on a JY ULTIMA 2. The samples were constitued of a mixture of 3 solvents (MeOH, EtOH, IsPrOH). The proportion of the 3 solvents are different from one sample to another one. We prepared a mixture of one third each MeOH, EtOH and IsPrOH to optimize the plasma, estimate the limits of detection and use as a rinsing solution. The specifications of the instrument are listed below in Tables 1 and 2.

Table 1: Specification of spectrometer

Parameters	Specifications
Mounting	Czerny Turner
Focal length	1m
Nitrogen purge	Yes
Variable resolution	Yes
Grating number of grooves	2400 gr/mm
Order	2nd order

Table 2: Specification of RF Generator

Parameters	Specifications
Type of generator	Solid state
Observation	Radial
Frequency	40.68 MHz
Control of gas flowrate	by computer
Control of pump flow	by computer
Cooling	air

The operating conditions are listed in Table 3 below.

Table 3: Operating conditions

Parameters	Conditions
RF Generator power	1400 W
Plasma gas flowrate	18 L/min
Auxiliary gas flowrate	1 L/min
Sheath gas flowrate	0.65L/min
Nebulizer flowrate	0.42 bars, 0.2 mL/min
Pump tubing	orange/white (solvflex)
Pump speed	13 rpm
Type of nebulizer	Meinhard K3 type
Type of spray chamber	Cyclonic
Argon humidifier	No
Injector tube diameter	3.0 mm

4 Semi-quantitative results

To know the level of each element, a semi-quantitative method was used. The calibration was made with two points for all elements: 0 and 5 mg/L. The blank was made by a mixture of one third each MeOH, EtOH and IsPrOH. This blank solution is used for the rinsing solution and for the calibration sandards.
Results of sample A are given in Table 4, as well as sample A + spike.

Semi-quantitative analyses are made with an error of about 20%. The recovery factor is within this error so the matrix effect can be considered as minor, and the results a good approximation of the real concentrations.

Note the very good recovery for Na, which is an illustration of linearity and easy analysis of alkaline elements using one single method.

Table 4: Sample A

	Wavelength (nm)	Sample A Concentration (mg/L)	Sample A + spike Measured concentration (mg/L)	Sample A + spike Theoretical concentration (mg/L)	Recovery %
As	189.042	< LOQ	0.478	0.5	95.6
Ca	317.933	0.124	0.742	0.624	118.9
Cd	228.802	< LOQ	0.394	0.5	78.8
Cr	267.716	< LOQ	0.41	0.5	82
Cu	324.754	0.0475	0.564	0.55	111.7
Hg	194.163	< LOQ	0.357	0.5	70.3
Na	589.592	12.83	73.79	72.83	101.3
Pb	220.353	< LOQ	0.363	0.5	72.6

LOQ = 3.3 x LD (LD from semiquant is considered as 3 times LD of table 10).

5 Quantitative results

Other elements have been requested afterwards : K, Ni and Zn. They will be analyzed in the same method. The samples were measured using the standard addition method (fully controlled by the Analyst software). The addition to sample A are listed in Table 5. Concentrations are expressed in mg/L.

Table 5: Standard Addition

	Add 0 mg/L	Add 1 mg/L	Add 2 mg/L	Add 3 mg/L
Ca	0	0.125	0.25	0.5
Cu	0	0.1	0.2	0.4
Na	0	2.5	5	10
Ni	0	0.01	0.02	0.04
K	0	0.125	0.25	0.5
Zn	0	0.01	0.02	0.04

Sample A is the unknown sample. Standard addition method was made using Add 0 to Add 3 in sample A. Then the sample A is determined as well as the spiked sample A, sample B and spiked sample B.

The results of sample A and B are in Table 6 and 7.

Table 6: Sample A, quantitative results

	Wavelength (nm)	Concentration (mg/L)	Sample A + spike Meas. concentration (mg/L)	Theoretical concentration (mg/L)	Recovery (%)
Ca	317.933	0.185	0.597	0.685	87.2
Cu	324.754	0.272	0.811	0.772	105.1
Na	589.592	76.816	125.671	121.816	103.2
Ni	231.604	0.041	0.612	0.541	113.12
K	766.490	4.193	5.987	6.193	96.67
Zn	213.856	0.011	0.455	0.511	89

Table 7: Sample B, quantitative results

	Wavelength (nm)	Concentration (mg/L)	Sample B + spike Meas. concentration (mg/L)	Theoretical concentration (mg/L)	Recovery (%)
Ca	317.933	0.189	0.70	0.689	101.6
Cu	324.754	0.156	0.703	0.656	107.2
Na	589.592	27.50	76.73	72.5	105.8
Ni	231.604	0.008	0.55	0.5008	109.82
K	766.490	0.258	2.078	2.258	105.8
Zn	213.856	0.008	0.444	0.5008	88.7

Recovery factors are between 85 and 110%; this demonstrates that all samples can be analyzed using one sample for calibration. For the elements not detected in the solutions, a calibration with 0 and 1 mg/L in sample A was done and the spiked samples (0.5 mg/L) were analyzed (Tables 8 and 9).

Table 8: Spiked sample B

	Wavelength (nm)	Concentration (mg/L)	Recovery (%)
As	189.042	0.561	112.20
Cd	226.502	0.544	108.80
Cd	228.802	0.538	107.60
Cr	267.716	0.536	107.20
Hg	194.163	0.518	103.60
Pb	220.353	0.611	122.20

Table 9: Spiked sample B

	Wavelength (nm)	Concentration (mg/L)	Recovery (%)
As	189.042	0.549	109.8
Cd	226.502	0.525	105.00
Cd	228.802	0.531	106.2
Cr	267.716	0.538	107.60
Hg	194.163	0.457	91.40
Pb	220.353	0.528	105.60

The recoveries are acceptable and validate the full methodology employed.

6 Limits of detection

Limits of detection were estimated using the formula LD = 3 x SD_0 with SD_0 : standard deviation over 10 replicates of blank analysis.

Table 10: Limits of Detection

	Wavelength (nm)	LD (µg/L)
As	189.042	15.25
Ca	317.933	7.27
Cd	226.502	0.98
Cd	228.802	0.78
Cr	267.716	1.49
Cu	324.754	3.01
Hg	194.163	4.26
K	766.490	351
Na	589.592	66.15
Ni	231.604	3.47
Pb	220.353	10.91
Zn	213.856	3.44

Limits of detection can be further improved with the use of a cooled spray chamber to remove the solvent.

7 Conclusion

The torch configuration (vertical torch, radial observation, sheath gas) allows easy analysis of the incineration solvents mixture. There is no requirement for dilution, cooled spray chamber or additional gases. The optimization was done on the plasma conditions and the sample uptake. The plasma and acquisition parameters are fixed in the analytical method and automatically controlled by computer for an optimum reproducibility from one operator to the other.

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