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**Investigation of a Method for
Multielement Determination
with OPTIMA 4300 (ICP-OES)**

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Abstract

We have studied and optimized the analytical conditions for quick, multielement analysis by inductively coupled plasma optical emission spectrometry (ICP-OES). The detection limits (LD) of 47 elements measured in total at 100 wavelengths have been evaluated for both plasma viewing modes; for axial viewing the LD vary from 0.00009 to 0.1 $\mu\text{g/g}$. The axial plasma offered an approximately 1 ~ 83-fold improvement in detection limits, while the radial plasma maintained a superior linear dynamic range. Using a dual view plasma instrument to measure waste water samples we got coincident results. The RSD was between 0.1% to 15% by axial view and about 1% to 30% by radial view.

After a series of different blank preparations and measurement by ICP-OES, we found that the source of a high Al blank signal was the automatic sampling system (Dispensette HF). To check possible interferences concentrated matrix solutions of Fe, Pb and $\text{Li}_2\text{B}_4\text{O}_7$ materials have been prepared partly by pressurized microwave digestion. The effect of the matrix interferences at 100 wavelengths of the multielement method have been discussed qualitatively.

Key words: *Inductively coupled plasma-optical emission spectrometry (ICP-OES), interference, Waste-water, Multielement, Al-contamination, Microwave digestion*

Untersuchung einer Methode zur Multielementanalyse mit dem ICP-OES-Gerät OPTIMA 4300

Kurzfassung

Die analytische Kapazität eines neuen ICP-OES-Gerätes wurde anhand einer Multielementanalyse von wässrigen Proben untersucht und optimiert. Die Erfassungsgrenzen von 47 Elementen und insgesamt 100 Emissionslinien wurden für zwei Plasmabeobachtungen ermittelt; für die axiale Beobachtung liegen sie im Bereich von 0,00009 bis 0,1 $\mu\text{g pro g}$ Lösung. Die axiale Plasmabeobachtung ermöglicht bis zu 83 mal bessere Erfassungsgrenzen als die radiale Plasmabeobachtung; letztere verfügt über einen größeren linearen Messbereich. Mit beiden Beobachtungsweisen wurden in einer Abwasserprobe übereinstimmende analytische Daten erzielt. Die Standardabweichung von Wiederholmessungen für die axiale Beobachtung liegen zwischen 0,1 und 15 % relativ und für die radiale zwischen 1 und 30 % relativ.

Nach einer Serie unterschiedlich hergestellter Säureblindwerte und deren ICP-OES Messungen wurde ein automatischer Dispenser (Dispensette) als Quelle für hohe Al Blindwerte festgestellt. Zur Untersuchung möglicher Interferenzen wurden konzentrierte Fe-, Pb- und $\text{Li}_2\text{B}_4\text{O}_7$ -Lösungen, zum Teil unter Einsatz eines Mikrowellendruckaufschlusses, hergestellt. Die Auswirkung möglicher spektraler Störungen dieser Matrixlösungen auf die 100 Emissionslinien der Multielementmethode qualitativ diskutiert.

1. Introduction

After the first commercial ICP-OES instruments were introduced to the analytical community in the 1980's, they have been applied to a wide variety of fields such as agricultural-, food-, biological- and clinical-, geological- and environmental science. Metals and organics were investigated and the success of the method was mainly due to its ability to achieve both low detection limits and trace multielement analyses rapidly. Perkin-Elmer Optima 4300DV ICP-OES is the newest system, which permits the use of different data collection and processing techniques than those used for traditional optical spectrometers which use an exit slit and photomultiplier tube in the focal plane. While the default parameter selected for the system provides an excellent performance, there are special cases where the performance may be improved further by invoking optional data collection and processing techniques.

The goals of this study are: (1) to determine the effects of some of these data collection and processing options on the detection limits (LD) and analyse the precision for the Optima 4300DV and to discuss the instrument's short-term and long-term stability; (2) to compare the LOD's of axial and radial plasma viewing; (3) the application of the multielement method to analyse a waste water sample; (4) to look for a possible source of Al-contamination as seen in a number of different samples measured in our lab; (5) to investigate possible interferences of the high concentrated Fe, Pb and $\text{Li}_2\text{B}_4\text{O}_7$, which always existed as the matrix by spectra examination; (6) to study on the solid sample decompositions with pressurized wave-digestion system.

Fig.1 shows a periodic table representation of the elements that can be determined by ICP-OES. A schematic of diagram the Optima 4300DV instrument is shown in Fig.2. The sample is usually transported into the instrument as a liquid. In a spray chamber the liquid is converted into an aerosol by a process known as nebulization. The sample aerosol is then transported into the plasma where many processes such as aerosol drying, sample evaporation, atomisation and excitation are induced by the transfer of energy from the RF-field to the electrons in the plasma and then to the sample components. The excited atoms and ions emit characteristic radiation which is dispersed, in this case, by an echelle polychromator. The radiation is detected by a two-dimensional Segmented-array Charge-coupled Device Detector (SCD) converting the incoming photons into electrons for measurement. By measuring standard solutions with known elements concentration at the same time as the sample solutions, quantitative analysis is achieved.

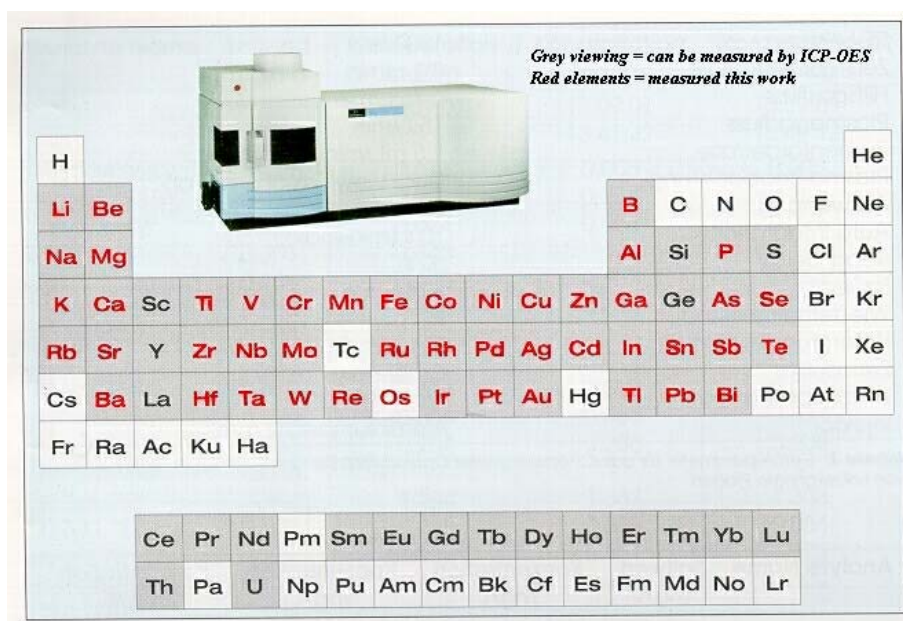


Fig.1 Periodic table with ICP-OES analysis

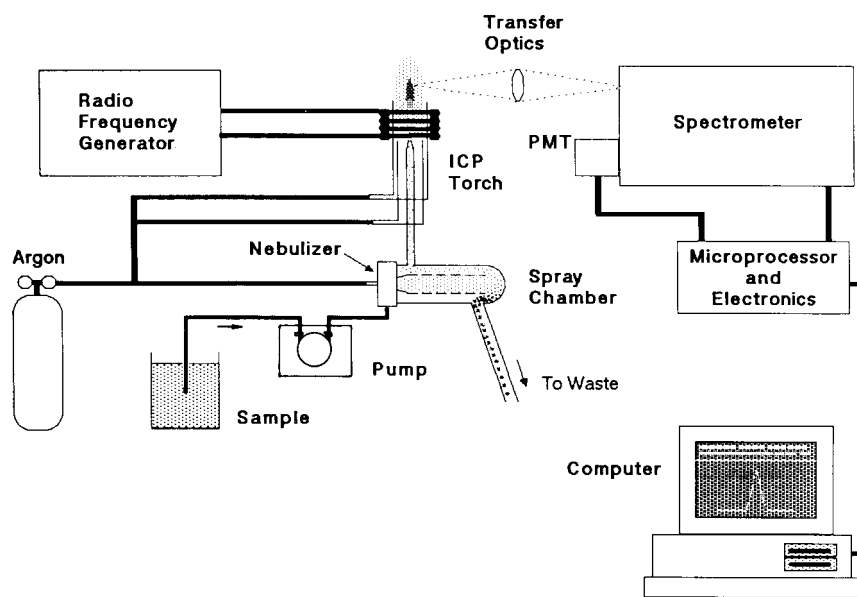


Fig.2 Major components and layout of a typical ICP-OES instrument

2. Experiments

2.1 ICP-OES Operating Parameters

A Perkin-Elmer Optima 4300 DV inductively coupled plasma optical emission spectrometer (ICP-OES) was used. The argon plasma source is powered by an RF generator. There are two kinds of photon detectors: one is an SCD array, covering an extended ultraviolet wavelength range from 165 to 403 nm. The VIS detector – a filter detector - covers the visible wavelength range from 404 to 782 nm. Both allow the simultaneous analysis of approximately 5000 analytical emission lines. A Ryton double-pass Scott-type spray chamber and the GemTip Cross-Flow pneumatic nebulizer are the standard components supplied with the instrument. Additionally a Perkin-Elmer AS-90+ autosampler was also used for sampling. The instrument is computer controlled using WinLab32™-Software. Table 1 lists the operating parameters.

Table 1 ICP-OES Operating Parameters

Parameter setting for	Al analysis	Multi_47elements Analysis axial view	Multi_47elements Analysis radial view
RF Power	1300 W		
Nebulizer Ar gas flow	0.75 L/min	0.75 L/min	0.75 L/min
Auxiliary Ar gas flow	0.2 L /min		
Plasma Ar gas flow	15 L/min		
Sample and wash flow rate	1.00 mL/min	1.20 mL/min	1.20 mL/min
Wash time	60 s	90 s	90 s
Sample read delay time	65 s	60 s	60 s
Resolution	High	Normal	Normal
Processing mode	Peak area		
Background	Manual selection of points		
Optical viewing	Axial	Axial	Radial
Replicate measurements	3	3	3

2.2 Reagents and blanks

2.2.1 Reagents

- HNO₃ (analytical grade, Merck) (65 %);
- HCl (analytical grade, Merck) (32 %);
- Diluted (1:10) HNO₃: 1 L HNO₃ (2.2.1 a) diluted with water to 10 L;
- HNO₃ (super-pure, Merck) (65 %);
- HCl (super-pure, Merck) (30 %);
- HF (super-pure, Merck) (40 %);
- 1,3% HNO₃: 2 mL HNO₃ (2.2.1 d) per 100 g solution;
- 2,6% HNO₃: 4 mL HNO₃ (2.2.1 d) per 100 g solution;
- 1,4% HCl: 4 mL HCl (2.2.1 e) per 100 g solution;
- 0,4% HF: 1mL HF (2.2.1 f) per 100 g solution.

2.2.2 Procedure to Wash PE (Poly-Ethylene) Bottles

As the sensitivity of the ICP-OES measurement is very high (i.e. < 1 ng/mL), solution contamination should be avoided and the containers and bottles where sample solution were stored or prepared have been cleaned by the following procedure:

- Wash by a washing machine (Miele, mielabor G7733) using de-ionised water;

- b. Fill a second wash solution composed of 200 mL HNO₃ (2.2.1 a), 100 mL HCl (2.2.1 b) in and 3700 ~ 4200 mL H₂O in a 4000 ~ 4500 mL beaker;
- c. Heat the beaker containing the bottles within the wash solution to 70 °C for approximately 3 h using the warm plate;
- d. Switch off the warm plate and keep the bottles in the washing solution over night;
- e. 24 h later, take out the bottles from the washing solution and wash 5-6 times with de-ionized water;
- f. Wash again with Millipore water;
- g. Dry the plastic bottles in the laminar flow hood.

2.2.3 Procedure to Wash Teflon FEP(Fluorinated Ethylene Propylene) Bottles

For preparation and storage of calibration solutions (standards) FEP bottles are recommended:

- a. Wash with Millipore water (once for new ones; three times for the used ones);
- b. Fill with diluted (1:10) HNO₃ (2.2.1c) and keep the bottles in a big vessel for 24 hours;
- c. Wash again with Millipore water 5-6 times;
- d. Dry the Teflon FEP bottles in the laminar flow hood.

2.2.4 Blank sample preparation using Dispensette for investigating Al-contamination

For sample and standard preparation HNO₃ (2.2.1 d), HCl (2.2.1 e) and HF (2.2.1 f) was dispensed by two kinds of Dispensettes (Fig.3 and Fig.4) attached to the bottles of super-pure acids.



Fig.3 Automatic Sampling (Dispensette) for HF



Fig.4 Automatic Sampling (Dispensette) for HCl and HNO₃

- a. Different amounts of acid were dispensed from the Dispensette into the PE bottles containing Millipore water for preparing the blank samples as shown in Table 9;
- b. Five days after first dispensing acid, having left acid in contact with the Dispensette material, a further series of blank samples were prepared as in a;
- c. After press Dispensette 10 times to keep acid in bottles, than take the acid with Dispensette to prepare the blank samples again.

2.2.5 Reagent blanks preparation for experiment 2.2.4

Reagent blanks for the above blank preparations were made from the same acid bottle on which the Dispensette had been attached, but, PE Pasteur Pipettes were used for sampling or

pipetting the acids. The blank solutions were diluted with Millipore water and stored in PE bottles.

2.3 Standard solution preparation

2.3.1 Al single standard

Aluminium single standard solutions (Merck) were successively diluted using PE bottles and the acid concentration was always adjusted to 1,3% HNO₃ (2.2.1 g)

Table 2 Al Standard Solution Preparation

Al standard solution	Al-EP1	Al-EP2	Al-EP3	Al-EP3
Concentration (µg/g)	0.0500	0.1020	0.1971	0.5046

2.3.2 Multielement standard solutions preparation

Calibration standards were made from single element standard solutions with a certified element concentration of approximately 1000 mg/L. All solutions were acidified to an acid concentration of 1,3% HNO₃ (2.2.1 g), 2,6% HNO₃ (2.2.1 h), 1,4% HCl (2.2.1 i), or 1,4% HCl (2.2.1 i) + 0,4% HF (2.2.1 j).

Table 3 Mass Content of Elements in Calibration Standard (Multi_006f2002)

ICP-Multi (Std6)					
Element	ICP-Multi Standard Con (µg/g)*	EP1(Std6) (µg/g)	EP2(Std6) (µg/g)	EP3(Std6) (µg/g)	EP4(Std6) (µg/g)
Ag	50	1,027	0,514	0,206	0,053
Al	150	3,082	1,542	0,617	0,159
B	15	0,308	0,154	0,062	0,016
Ba	5	0,103	0,051	0,021	0,005
Be	1	0,021	0,010	0,004	0,001
Bi	200	4,109	2,056	0,823	0,212
Cd	20	0,411	0,206	0,082	0,021
Co	20	0,411	0,206	0,082	0,021
Cr	25	0,514	0,257	0,103	0,026
Cu	20	0,411	0,206	0,082	0,021
Fe	15	0,308	0,154	0,062	0,016
Ga	150	3,082	1,542	0,617	0,159
In	200	4,109	2,056	0,823	0,212
Mn	5	0,103	0,051	0,021	0,005
Ni	50	1,027	0,514	0,206	0,053
Pb	200	4,109	2,056	0,823	0,212
Sr	1	0,021	0,010	0,004	0,001
Tl	400	8,218	4,112	1,646	0,424
Zn	20	0,411	0,206	0,082	0,021
HNO3		4 %			

* ICP-multi-element standard solution (19 elements), Merck company

Table 4 Mass Content of Elements in Calibration Standard (Multi_006f2002)

Nonmetal-Multi (Std1)							
Element	Single Standard Con (µg/mL)	Company	EP1(Std1) (µg/g)	EP2(Std1) (µg/g)	EP3(Std1) (µg/g)	EP4(Std1) (µg/g)	
As	995	Merck	2,005	1,072	0,500	0,110	
Te	1000	Alfa	2,015	1,077	0,503	0,111	
Sb	1000	Alfa	2,015	1,077	0,503	0,111	
P	1000	Merck	1,008	0,539	0,251	0,055	
Sn	1000	Alfa	1,008	0,539	0,251	0,055	
Se	1000	Merck	1,008	0,539	0,251	0,055	
HCl						1,4%	
HF						0,4%	
Refractory-Multi (Std2)							
Element	Single Standard Con (µg/mL)	Company	EP1(Std1) (µg/g)	EP2(Std1) (µg/g)	EP3(Std1) (µg/g)	EP4(Std1) (µg/g)	
W	1000	Alfa	1,000	0,501	0,250	0,050	
Nb	1000	Alfa	0,100	0,050	0,025	0,005	
Ta	1000	Alfa	0,100	0,050	0,025	0,005	
Mo	1000	Alfa	0,100	0,050	0,025	0,005	
V	1000	Merck	0,100	0,050	0,025	0,005	
Zr	1000	Alfa	0,100	0,050	0,025	0,005	
Hf	1000	Alfa	0,100	0,050	0,025	0,005	
Ti	999	Merck	0,020	0,010	0,005	0,001	
HCl						1,4%	
HF						0,4%	
Alkali-Multi (Std3)							
Element	Single Standard Con (µg/mL)	Company	EP1(Std1) (µg/g)	EP2(Std1) (µg/g)	EP3(Std1) (µg/g)	EP4(Std1) (µg/g)	
Li	1000	Merck	1,001	0,500	0,250	0,050	
Na	1000	Alfa	1,001	0,500	0,250	0,050	
K	998	Merck	0,999	0,499	0,249	0,050	
Rb	1000	Alfa	1,001	0,500	0,250	0,050	
Ca	1001	Merck	0,100	0,050	0,025	0,005	
Ba	1000	Merck	0,100	0,050	0,025	0,005	
Mg	1000	Merck	0,020	0,010	0,005	0,001	
Sr	1000	Merck	0,020	0,010	0,005	0,001	
HNO3						2,6%	
Steel-Multi (Std4)							
Element	Single Standard Con (µg/mL)	Company	EP1(Std1) (µg/g)	EP2(Std1) (µg/g)	EP3(Std1) (µg/g)	EP4(Std1) (µg/g)	
Bi	1002	Merck	1,003	0,501	0,252	0,051	
Pb	1001	Merck	1,002	0,500	0,252	0,051	
Ag	1002	Merck	0,101	0,050	0,025	0,005	
Al	999	Merck	0,100	0,050	0,025	0,005	
Cr	996	Merck	0,100	0,050	0,025	0,005	
B	1001	Merck	0,101	0,050	0,025	0,005	
Cu	1000	Alfa	0,100	0,050	0,025	0,005	
Ni	1000	Alfa	0,100	0,050	0,025	0,005	
Zn	1000	Merck	0,100	0,050	0,025	0,005	
Co	1000	Alfa	0,020	0,010	0,005	0,001	
Cd	1000	Merck	0,020	0,010	0,005	0,001	
Fe	1001	Merck	0,020	0,010	0,005	0,001	
Mn	1000	Merck	0,020	0,010	0,005	0,001	
HNO3						2,6%	
Noble-Multi (Std5)							
Element	Plasma Standard Con (µg/mL)	Company	EP1(Std1) (µg/g)	EP2(Std1) (µg/g)	EP3(Std1) (µg/g)	EP4(Std1) (µg/g)	
Au, Ir, Os, Pd, Pt, Re, Rh, Ru	100ug/mL	Alfa	0,201	0,100	0,050	0,010	
HCl						1,4%	

2.4 Waste-water sample preparation

Waste-water samples, which came from an experimental laboratory from ITC-TAB in FZK were well shaken and acidified to 2,6% HNO₃ or diluted with 2,6%HNO₃, individually.

2.5 Decomposition of matrix samples for the investigating the matrix interferences

(Method 1, Method 2 and Method 3)

In order to investigate possible interferences of the matrix solutions by spectra examination, we prepared the pure Fe, Pb, $\text{Li}_2\text{B}_4\text{O}_7$ (Spectromelt 10A) and Steel solutions as below procedure.

2.5.1 Dissolution of matrix samples without microwave (Method 1)

- Accurately weigh Iron powder, Steel, Lead shot and $\text{Li}_2\text{B}_4\text{O}_7$ about 1.0000 g into the PE bottles;
- Add 10mL Millipore water, add 10mL HNO_3 (2.2.1 d) dropwise to the sample to keep reaction, in the meantime shake the bottle;
- Put the bottle in the water-bath to heat approximately at 90 °C about 3 hours;
- Cool to room temperature;
- Dilute to 100 g with Millipore water.

2.5.2 Dissolve matrix samples using microwave system (Method 2 and Method 3)

Steel and Iron power matrix samples were prepared by pressurized microwave digestion using a MULTIWAVE microwave sample preparation system:

- Accurately weight 0,5000 g Iron powder and Steel sample into the Teflon PFA liner;
- Add 6 mL HNO_3 (2.2.1 d) (Method 2) or drop 6 mL aqua regia (Method 3) to the samples;
- Allow the pre-reaction for approximately 3 hours;
- Cap the vessel in the capping station;
- Digest following the procedure in Table 5;
- Cool for five minutes, vent and open the vessels;
- Transfer the samples into PE bottles and dilute to 50 g with Millipore water.

Table 5 Microwave Digestion Parameters for Steel analysis

Step	Power(w)	Time(min)	Max Temperature(°C)	Fan
1	200	5	150	1
2	900	25	280	1
3	0	15	120	3
4	0	0	room temperature	0
5	0	0	room temperature	0
6	0	0	room temperature	0

2.6 ICP-OES analyses

In general, the samples were analysed by ICP-OES with the following procedure:

- After checking system connection, open argon gas, ignite plasma;
- After stabilization of 72 minutes, measure 1 $\mu\text{g/mL}$ Mn standard solution to check the instrument sensitivity and stability (above 1.2×10^5 cps per 1 $\mu\text{g/mL}$, RSD less than 0.6 %);
- Begin to analyse calibration blanks, standards, samples and again blank, standard as samples to check and to exclude a possible drift of the instrument;
- After the last sample was measured, measure 1 $\mu\text{g/mL}$ Mn standard solution again to check the instrument sensitivity and stability;
- Wash instrument with diluted 1,3% HNO_3 15 min and Millipore water for 10 min;
- Turn off plasma, close argon gas.

According to the ICP-OES operating parameters shown in Table 1 , following samples are measured individually: Al blank samples; Multi-elements in waste-water samples (Axial and Radial viewing); Multi-elements in 1000 µg/g solution (µg/g Sol), 5000 µg/g Sol and 10000 µg/g Sol high pure iron; 10000 µg/g Sol steel; 10000 Pb µg/g Sol and 10000 Li₂B₂O₇ µg/g Sol matrix samples.

Table 6 - Table 9 depict the wavelengths, background correction and points per peak for 47 elements analysis using dual viewing method.

Table 6 Wavelengths, Background Correction and Points per Peak for 47elements Analysis (Axial)

Element	Emission wavelength (nm)	Background Correction (nm)		Points per peak	Element	Emission wavelength (nm)	Background Correction (nm)		Points per peak
		BGC1 (-)	BGC2 (+)				BGC1 (-)	BGC2 (+)	
Ag	328,068	0,020	0,021	3	Ni	221,648	0,027		3
	338,289		0,054			231,604			
Al	237,313	0,048	0,036	3	Os	225,585	0,014		3
	394,401		0,060			228,226			
As	396,153	0,029	0,067	3	P	177,434	0,017	0,011	3
	188,979		0,034			178,221			
Au	193,696	0,015	0,013	3	Pb	213,617	0,020		3
	242,795		0,014			214,914			
B	267,595	0,031	0,034	3	Pd	217,000	0,014	0,013	3
	182,528		0,011			220,353			
Ba	249,677	0,033	0,026	3	Pt	405,781	0,041	0,056	3
	249,772		0,025			340,458			
Be	233,527	0,021	0,022	3	Rb	363,470		0,033	3
	455,403		0,051			214,423			
Bi	313,042	0,031	0,025	3	Re	265,945	0,009	0,016	3
	313,107		0,017			780,023			
Ca	190,171	0,035	0,023	3	Rh	197,248	0,016		3
	222,821		0,014			204,908			
Cd	223,061	0,068	0,016	3	Ru	204,908	0,018	0,011	3
	315,887		0,066			227,525			
Co	317,933	0,047	0,065	3	Sb	233,477	0,021	0,031	3
	393,366		0,025			343,489			
Cr	214,440	0,025	0,021	3	Se	240,272	0,015	0,019	3
	228,802		0,021			349,894			
Cu	228,616	0,014	0,020	3	Sn	206,836	0,013	0,015	3
	238,892		0,015			217,582			
Fe	205,560	0,018	0,022	3	Sr	231,146	0,016	0,036	3
	267,716		0,025			196,026			
Ga	221,459	0,054	0,034	3	Te	203,985	0,013		3
	324,752		0,020			189,927			
Hf	327,393	0,057	0,020	3	Ti	235,485	0,014		3
	238,204		0,043			283,998			
In	239,562	0,021	0,021	3	Tl	407,771	0,068	0,054	3
	259,939		0,051			421,552			
Ir	294,264	0,016	0,051	3	V	226,230	0,041	0,009	3
	417,206		0,009			240,063			
K	232,247	0,028	0,027	3	W	214,281	0,014	0,020	3
	277,336		0,034			238,578			
Li	303,936	0,036	0,027	3	Zn	334,940	0,093	0,030	3
	325,609		0,030			336,121			
Mg	224,268	0,035	0,040	3	Zr	190,801	0,012	0,024	3
	766,490		0,141			276,787			
Mn	670,784	0,183	0,141	3	Zr	290,880	0,019	0,019	3
	285,213		0,056			310,230			
Mo	257,610	0,026	0,026	3	Zr	207,912	0,019	0,018	3
	259,372		0,025			224,876			
Na	202,031	0,025	0,019	3	Zr	206,200	0,017	0,014	3
	203,845		0,013			213,857			
Nb	589,592	0,090	0,125	3	Zr	339,197	0,021	0,021	3
	309,418		0,019			343,823			
	313,079	0,038	0,038	3					

Table 7 Wavelengths, Background Correction and Points per Peak for 47elements Analysis (Radial)

Element	Emission wavelength (nm)	Background correction (nm)		Points per peak	Element	Emission wavelength (nm)	Background correction (nm)		Points per peak
		BGC1	BGC2				BGC1	BGC2	
Ag	328,068	0,02	0,021	3	Ni	221,648	0,011		2
	338,289		0,021	3		231,604	0,014		3
Al	237,313		0,036	3	Os	225,585		0,014	3
	394,401	0,107	0,06	3		228,226		0,015	3
As	396,153	0,048	0,061	3	P	177,434	0,014		3
	188,979	0,012	0,034	3		178,221	0,012	0,01	3
Au	193,696	0,013	0,013	3	Pb	213,617	0,033	0,013	3
	242,795	0,015	0,014	3		214,914	0,033	0,019	3
B	267,595	0,031	0,034	3	Pd	217,000	0,014	0,013	3
	182,528	0,013		3		220,353	0,015	0,019	3
Ba	249,677	0,013		3	Pt	405,781	0,05	0,048	3
	249,772	0,013		3		340,458	0,031	0,011	3
Be	233,527	0,021	0,022	3	Rb	363,470		0,033	3
	455,403	0,046	0,047	3		214,423	0,008		3
Bi	313,042	0,031	0,027	3	Re	265,945	0,009	0,016	3
	313,107	0,096		1		780,023	0,081		3
Ca	190,171	0,035	0,023	3	Rh	197,248	0,016		3
	222,821	0,014	0,014	3		204,908	0,018	0,011	3
Cd	223,061	0,016		3	Ru	227,525	0,02		3
	315,887	0,068		3		233,477	0,007	0,014	3
Co	317,933	0,066		3	Sb	343,489	0,012	0,021	3
	393,366	0,129		3		240,272	0,022	0,008	2
Cr	214,440	0,019		3	Se	349,894		0,033	3
	228,802	0,015	0,02	3		206,836	0,006	0,013	3
Cu	228,616	0,014	0,02	3	Sn	217,582	0,009	0,018	3
	238,892	0,014	0,022	3		231,146	0,014	0,021	3
Fe	205,560		0,011	3	Sr	196,026		0,012	3
	267,716	0,025	0,025	3		203,985		0,013	3
Ga	221,459		0,034	3	Ta	189,927		0,017	3
	324,752	0,04	0,04	3		235,485	0,014		3
Hf	327,393	0,03		3	Te	283,998	0,019	0,017	3
	238,204		0,043	3		407,771	0,068	0,039	3
In	239,562			3	Ti	421,552	0,057	0,059	3
	259,939			3		226,230	0,041	0,012	3
Ir	294,264	0,019	0,018	3	V	240,063	0,017	0,015	3
	417,206	0,039	0,014	1		214,281	0,011	0,017	3
K	232,247	0,022	0,014	3	W	238,578	0,008	0,019	3
	277,336	0,017	0,034	3		334,940	0,093	0,03	3
Li	303,936			3	Zn	336,121	0,021		3
	325,609	0,023	0,03	3		190,801	0,012	0,024	3
Mg	224,268		0,011	3	Zr	276,787	0,017	0,017	3
	766,490	0,16	0,158	3		290,880	0,017	0,019	3
Mn	670,784	0,183		3	Zr	310,230	0,018	0,02	3
	285,213	0,052	0,026	3		207,912	0,013	0,013	3
Mo	257,610			3	Zr	224,876	0,014	0,014	3
	259,372			3		206,200	0,017	0,014	3
Na	202,031	0,025	0,019	3	Zr	213,857		0,038	3
	203,845	0,013	0,019	3		339,197	0,021	0,021	3
Nb	589,592	0,143	0,125	3	Zr	343,823	0,021	0,021	3
	309,418	0,019		3					
	313,079		0,01	3					

3. Discussion and Conclusion

3.1 Al-contamination from the sample preparation procedure

After a series of blank sample analyses by ICP-OES, as shown in Table 6, the preliminary results concerning Al-contamination were as listed below:

- Acid blanks prepared by automatic sampling (Dispensette) gave a higher Al concentration than those prepared using a PE Pasteur Pipette by hand;
- Automatic HF sampling gave a higher intensity than HNO₃ and HCl;
- Al concentration increases with time for the Dispensette produced blanks;
- The higher Al background comes from the automatic sampling system (Dispensette HF).

The Dispensette HF which is in contact with the acid is made of Ceramic, Platinum-Iridium, ETFE (Ethylen-Tetrafluorethylen-Copolymer), PFA (Perfluoralkoxy- Copolymer), FEP (Perfluorethylenpropylen-Copolymer) and PP (Polypropylen). Whilst the Dispensette Organic is made of boro-silicate glass, Ceramic, Tantalum, ETFE, PFA, FEP and PP.

So aluminium is possibly leached from the Ceramic of the Dispensette system. The longer HF is kept inside the Dispensette, the more Al will be produced.

Table 6 Al Content in Blank Samples

Information of Samples	Sample ID	Int (Corr)	Conc (ug/g)	
Calib blank	blank(1,3%HNO3)	-13,3	0,00	
Al standard solution	Al-EP1	894,4	0,0500	
	Al-EP2	1811,4	0,1020	
	Al-EP3	3569,2	0,1971	
	Al-EP4	9093,6	0,5046	
Washing acid between samples	ore	-17,3		
Water, Millipore	BK-H2O	3,9	-	
BK, BKb -15.11.2001 Sample Weight: 50g BK = acid taken by hand with a PE tube	BK-5mlHNO3	67,9	-	
	BK-10mlHNO3	70,4	-	
	BK-4mlHF	268,0	-	
	BK-6mlHF	246,6	-	
	BK-3mlHCl	-35,4	-	
	BK-6mlHCl	212,6	-	
	BKb-HCl,HNO3=same acid taken by Dispensette(organic)	BKb-5mlHNO3	617,0	-
		BKb-10mlHNO3	179,2	-
	Bkb-HF=same acid taken by Dispensette(HF)	BKb-4mlHF	1786,0	0,112
		BKb-6mlHF	413,1	-
BKb-3mlHCl		911,1	0,051	
BKb-6mlHCl		346,0	-	
Autom - 09.11.2001 Autom..HF/HNO3 =acid taken by Dispensette(organic)	Autom4mlHF/50g	4474,1	0,301	
	Autom6mlHF/50g	8425,5	0,578	
	O.A. -13. 11. 2001 Sample Weight: 50g O.A. HNO3/HF acid taken by hand with a PE tube	O.A.4mlHF/50g	182,9	-
		O.A.6mlHF/50g	223,3	-
		O.A.5mlHNO3/50g	72,6	-
		O.A.10mlHNO3/50g	67,3	-
vor-first time to take acid nach-after press Dispensette 10 times to keep acid in bottle, than take acid by Dispensette	BK2vor-6mlHF/100g	221,7	-	
	BKb2vor-3mlHF/100g	1925,5	0,121	
	BKb2vor-6mlHF/100g	565,5	0,026	
	BKb2nach-3mlHF/100g	148,3	-	
	BKb2nach-6mlHF/100g	287,3	-	
	BK2nach-6mlHF/100g	293,1	-	
	BKb3-6mlHF/50g	582,1	-	

3.2 Correction coefficient and detection limits of 47 elements (100 analysis lines) in dual viewing by ICP-OES

The detection limits for plasma dual viewing, defined as 6 times the standard deviation of replicate measurements of calibration blank solutions, together with the linear dynamic range calibration correction coefficient (corr. coef.) are listed in Table 7. For axial viewing the LOD vary from 0.00009 to 0.1 ug/g. The axial plasma offered an approximately 1 ~ 83-fold improvement in detection limits, while the radial plasma maintained a superior linear dynamic range.

Table 7 Correction Coefficient and Limit of Detection (LOD) Relative to Wavelengths

Element	Emission wavelength (nm)	Axial		Radial		LOD _R	Element	Emission wavelength (nm)	Axial		Radial		LOD _R	
		corr coef	LOD (ug/g)	corr coef	LOD (ug/g)	LOD _X			Corr Coef	LOD (ug/g)	corr coef	LOD (ug/g)	LOD _X	
Ag	328.068	0.9999	0.0014	1.0000	0.023	16	Ni	221.648	1.0000	0.0022	1.0000	0.011	5	
	338.289	0.9998	0.0063	1.0000	0.034	5		231.604	0.9997	0.0032	1.0000	0.024	8	
Al	237.313	0.9999	0.0046	0.9999	0.24	51	Os	225.585	0.9969	0.0032	0.9952	0.033	10	
	394.401	0.9998	0.010	0.9999	0.0050	0		228.226	0.9969	0.0050	0.9975	0.053	10	
As	188.979	1.0000	0.012	0.9996	0.31	25	P	177.434	0.9999	0.022	-	-	-	
	193.696	1.0000	0.031	0.9992	0.23	7		178.221	0.9998	0.067	0.9062	1.21	18	
Au	242.795	0.9996	0.0015	0.9997	0.0077	5		213.617	1.0000	0.024	0.9999	0.14	6	
	267.595	1.0000	0.0026	0.9999	0.0076	3		214.914	0.9999	0.034	0.9983	0.29	9	
B	182.528	0.9995	0.0034	0.9425	0.049	15	Pb	217.000	0.9998	0.047	0.9992	0.28	6	
	249.677	0.9991	0.0070	0.9953	0.0032	0		220.353	0.9996	0.0086	0.9997	0.096	11	
	249.772	0.9991	0.0057	0.9954	0.0030	1		405.781	0.9993	0.022	0.9996	0.15	7	
Ba	233.527	0.9955	0.0006	0.9961	0.0029	5	Pd	340.458	0.9997	0.0099	0.9998	0.016	2	
	455.403	0.9966	0.00010	0.9954	0.00086	8		363.470	0.9681	0.30	-	-	-	
Be	313.042	0.9997	0.00035	0.9999	0.00040	1	Pt	214.423	1.0000	0.0016	0.9986	0.076	48	
	313.107	0.9999	0.00030	0.9998	0.00059	2		265.945	1.0000	0.0051	0.9996	0.030	6	
Bi	190.171	0.9998	0.027	0.9986	0.79	29	Rb	780.023	0.9996	0.050	0.7922	1.7	35	
	222.821	0.9998	0.0086	0.9997	0.21	24		Re	197.248	1.0000	0.0040	0.9963	0.060	15
	223.061	0.9996	0.0094	0.9996	0.075	8			204.908	0.9995	0.046	0.5943	2.7	59
Ca	315.887	0.9988	0.010	0.9950	0.083	8	227.525		1.0000	0.0021	0.9996	0.010	5	
	317.933	0.9990	0.0013	0.9997	0.011	9	Rh	233.477	1.0000	0.010	0.9976	0.063	6	
	393.366	0.9989	0.00011	0.9985	0.0007	6		343.489	0.9999	0.011	0.9997	0.014	1	
Cd	214.440	0.9999	0.00016	1.0000	0.0049	31	Ru	240.272	1.0000	0.0028	0.9998	0.0076	3	
	228.802	1.0000	0.00032	1.0000	0.0086	27		349.894	0.9995	0.030	0.9923	0.058	2	
Co	228.616	1.0000	0.0019	1.0000	0.0097	5	Sb	206.836	1.0000	0.0037	0.9998	0.073	20	
	238.892	0.9999	0.0011	1.0000	0.0035	3		217.582	1.0000	0.0042	0.9998	0.066	16	
Cr	205.560	0.9999	0.0022	0.9998	0.034	16		231.146	1.0000	0.0060	0.9999	0.19	32	
	267.716	0.9998	0.00067	0.9998	0.0042	6	Se	196.026	1.0000	0.036	0.9915	0.34	9	
Cu	221.459	0.9998	0.017	0.9976	0.13	8		203.985	1.0000	0.034	0.9913	0.23	7	
	324.752	0.9994	0.0025	0.9999	0.017	7	Sn	189.927	1.0000	0.010	0.9994	0.32	31	
Fe	327.393	0.9996	0.0048	0.9997	0.054	11		235.485	0.9999	0.015	0.9999	0.17	11	
	238.204	0.9996	0.00033	0.9999	0.0053	16		283.998	1.0000	0.042	0.9998	0.113	3	
	239.562	0.9998	0.0036	0.9999	0.0064	2	Sr	407.771	0.9946	0.00015	0.9960	0.0003	2	
	259.939	0.9998	0.0015	0.9998	0.0017	1		421.552	0.9947	0.0002	0.9956	0.0012	7	
Ga	294.264	0.9998	0.021	1.0000	0.023	1	Ta	226.230	0.9998	0.0063	0.9845	0.031	5	
	417.206	0.9997	0.015	1.0000	0.18	13		240.063	1.0000	0.0020	0.9998	0.005	2	
Hf	232.247	1.0000	0.0011	0.9994	0.028	25	Te	214.281	1.0000	0.019	1.0000	0.059	3	
	277.336	1.0000	0.0012	0.9988	0.0096	8		238.578	1.0000	0.064	0.9999	0.17	3	
In	303.936	0.9999	0.11	1.0000	0.09	1	Ti	334.940	0.9999	0.0002	0.9999	0.0007	3	
	325.609	0.9999	0.058	1.0000	0.035	1		336.121	1.0000	0.0020	0.9997	0.0014	1	
Ir	224.268	1.0000	0.00420	0.9972	0.031	7	Tl	190.801	1.0000	0.007	0.9999	0.45	64	
	K	766.490	0.9998	0.010	0.9974	0.15		15	276.787	0.9999	0.010	1.0000	0.12	12
Li		670.784	0.9998	0.00018	0.9999	0.011	57	V	290.880	0.9997	0.009	0.9998	0.0040	0
	Mg	285.213	0.9999	0.00042	0.9998	0.0013	3		310.230	1.0000	0.023	1.0000	0.0052	0
Mn		257.610	0.9996	0.00009	0.9998	0.00041	5	W	207.912	1.0000	0.0012	0.9995	0.10	83
	259.372	0.9996	0.0011	0.9997	0.00043	0	224.876		1.0000	0.0046	0.9997	0.082	18	
Mo	202.031	1.0000	0.0015	0.9999	0.032	22	Zn	206.200	0.9999	0.0004	0.9998	0.017	42	
	203.845	0.9999	0.0090	0.9976	0.068	8		213.857	0.9997	0.0004	0.9998	0.0024	6	
Na	589.592	0.9999	0.0039	0.9997	0.15	38	Zr	339.197	1.0000	0.0018	1.0000	0.0019	1	
	Nb	309.418	0.9997	0.0052	0.9999	0.0027		1	343.823	1.0000	0.0018	1.0000	0.0022	1
313.079		0.9997	0.015	0.9999	0.0070	0								

It is clear that the axial configuration gives better detection limits than the radial. Fig.5 is a schematic diagram of the Optima 4300 DV optical system. The axial plasma is a horizontal ICP which is viewed from the end, produces higher analysed emission, improved sensitivity and LD. However, along with this enhancement, there are increased spectral interference problems and matrix-induced interferences. On the other hand, the radial plasma is viewed from the side, and has less interferences. So much thought must be given when deciding what viewing configuration to use when analysing more complicated samples. Generally, unless detection limit is the major criterion when analysing a set of samples, the radial-viewing configuration should always be the first option.

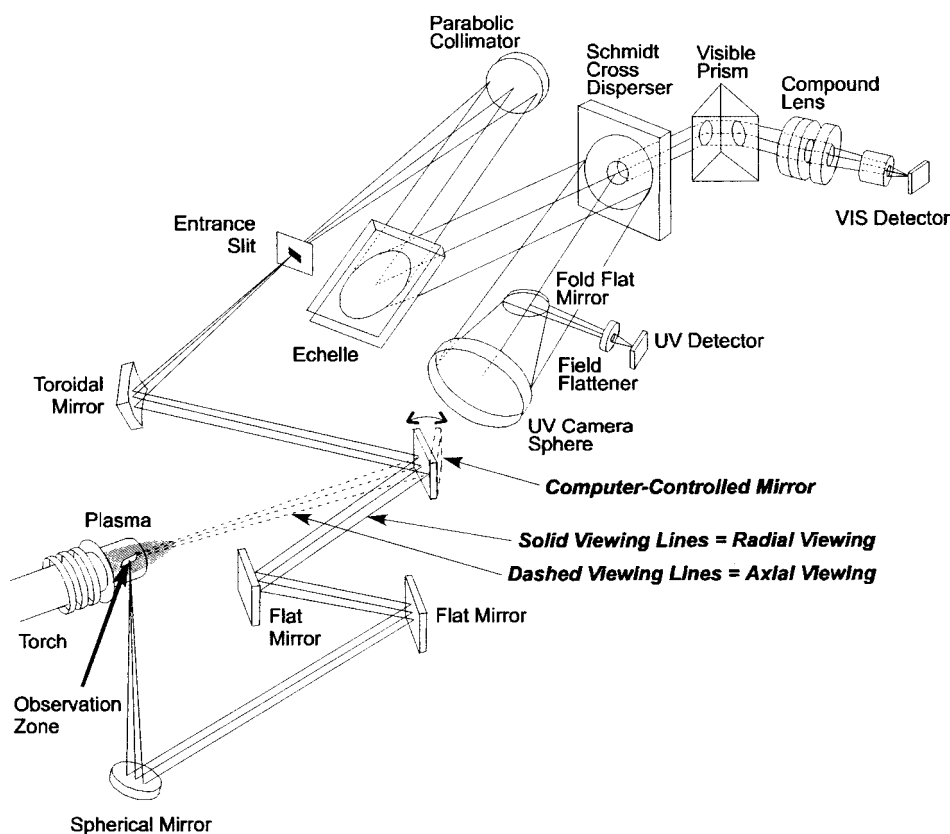


Fig.5 Schematic diagram of the Optima 4300 DV optical system

3.3 ICP-OES Instrument stability

Table 8 summarizes the intensities and the corresponding relative deviation of the Mn-check solution 1 $\mu\text{g/mL}$ before and after the multi-elements determinations. Data collection for three replicates requires approximately 6 minutes and as can be seen the short term precision is excellent, generally less than 0.6%; The relative standard deviation of both intensities (before and after) indicates a drift over three hours period to be less than 3.5% of RSD.

Table 8 Mn 257.610 Testing Results

Date	The Beginning		The End		Middle term precision	
	Corrected Intensity	RSD%	Corrected Intensity	RSD%	Mean Intensity	RSD%
14.01.2002	152078,2	0,25	156519,9	0,54	154299,1	1,44
15.01.2002	146871,5	0,23	150210,5	0,15	148541,0	1,12
23.01.2002	146351,7	0,14	155657,0	0,27	151004,4	3,08
24.01.2002	154314,9	0,23	153302,9	0,57	153808,9	0,33
25.01.2002	145952,4	0,16	145595,1	0,26	145773,8	0,12
07.02.2002	151830,5	0,05	141755,0	0,18	146792,8	3,43
20.02.2002	139413,2	0,04	144369,0	0,10	141891,1	1,75

3.4 Results of waste-water sample by ICP-OES

The results of the waste water investigation are presented in Table 9. Generally there is a very good agreement between the results of axial and radial measurements.

Table 9 Main Elements of Waste Water (sample number 006f2002)

Analysis Name	006f2002_Axial		006f2002_Radial	
	Mean (µg/mL)	SD	Mean (µg/mL)	SD
Ag 328.068	0,004	0,0001	ND	-
Al 396.153	47,0	0,3	45,6	1,2
As 188.979	0,19	0,003	0,23	0,04
Au 242.795	0,04	0,0001	0,04	0,0004
B 249.677	1,10	0,02	1,10	0,02
Ba 455.403	0,04	0,02	0,076	0,027
Be 313.107	0,002	0,000003	0,002	0,00005
Bi 190.171	0,20	0,002	ND	-
Ca 315.887	286	7,2	280	5,2
Cd 228.802	1,00	0,002	0,98	0,01
Co 228.616	0,028	0,00008	0,029	0,001
Cr 267.716	1,11	0,05	1,14	0,02
Cu 324.752	9,8	0,04	9,4	0,16
Fe 238.204	15,9	0,03	15,5	0,1
Ga 417.206	0,13	0,004	ND	-
Hf 232.247	ND	-	ND	-
Ir 224.268	ND	-	ND	-
In 325.609	ND	-	ND	-
K 766.490	386	12,9	334	4,3
Li 670.784	0,46	0,0009	0,29	0,003
Mg 285.213	35,0	1,1	33,3	0,5
Mn 257.610	3,4	0,01	3,3	0,02
Mo 202.031	0,15	0,002	0,20	0,001
Na 589.592	439	21,4	366	4,4
Nb 313.079	0,071	0,002	0,060	0,004
Ni 231.604	0,51	0,002	0,57	0,01
Os 225.585 or Os228.226	ND	-	ND	-
P 178.221	5,9	0,5	11,9	2,1
Pb 220.353	5,0	0,2	5,3	0,05
Pd 340.458	0,010	0,001	ND	-
Pt 265.945	0,073	0,0002	ND	-
Rb 780.023	2,8	0,03	ND	-
Re 197.248; Re204.908 or Re197.248	ND	-	ND	-
Rh 233.477 or Rh 343.489	ND	-	ND	-
Ru 240.272 or Ru 349.894	ND	-	ND	-
Sb 206.836	0,50	0,002	0,64	0,004
Se 196.026	ND	-	ND	-
Sn 189.927	0,084	0,004	ND	-
Sr 407.771	0,51	0,01	0,48	0,005
Ta 226.230 or Ta 240.063	ND	-	-	-
Te 214.281	ND	-	ND	-
Ti 334.940	0,97	0,005	0,92	0,03
Tl 190.801	0,036	0,003	ND	-
V 290.880	0,054	0,001	0,057	0,002
W 207.912	0,54	0,03	0,86	0,13
Zn 206.200	35,2	0,1	33,9	0,26
Zr 343.823	0,011	0,0002	0,013	0,0009

ND = Not Detected; Signal below the LOD (see Table 7)

3.5 Samples Decomposition

Obviously, Table 10 shows that lead and $\text{Li}_2\text{B}_4\text{O}_7$ can be dissolved using concentrated HNO_3 in open heating water-bath (Method 1). But for steel and high pure iron decomposition in pressurized microwave digestion system should be used with aqua regia complex acid (Method 3).

Table 10 Matrix Samples Decomposition Results

Matrix	Samole	Company	method 1	method 2	method 3
Fe	Iron powder, -22mesh, Puratronic, 99.998% EG-Nr.: 231-096-4 CAS: 7439.89-6 0/0	Alfa Aesar	No decomposition	No decomposition	complete decomposition
Steel	Analysen-Kontrollprobe 030-4/... 2421	BAM, MPI MPA	No decomposition	No decomposition	complete decomposition
Pb	Lead shot, 3mm (0.2in), 99.9999% (metal basis)	Alfa Aesar	complete decomposition		
$\text{Li}_2\text{B}_4\text{O}_7$	$\text{Li}_2\text{B}_4\text{O}_7$ M=169.12g/mol Spectromelt A10	Merck	complete decomposition		

The benefits of pressurized microwave digestion are:

- Intensified contact of sample and reagents;
- Shorter reaction times;
- Better recoveries;
- Easy to handle.

3.6 Matrix interferences in ICP-OES

Fig.6, 7 and 8 show the spectra of Al at 237.313nm, 394.401nm, 396.153nm of the standard solutions and Fe matrix solutions. All three spectra display the complex interferences and the stepwise elevated background caused by the 1000 $\mu\text{g/g}$, 5000 $\mu\text{g/g}$, 10000 $\mu\text{g/g}$ pure Fe and steel matrices. Qualitative results concerning Fe matrix interferences to 47 elements, as well as left and right beside 100 wavelengths, are summarized in Table 11. In comparison to the Fe and steel solutions, neither the background of 10000 $\mu\text{g/g}$ pure Pb or 10000 $\mu\text{g/g}$ $\text{Li}_2\text{B}_4\text{O}_7$ solutions is raised, nor do other emission lines interfere with the analysed line; see Fig.9. qualitative results about Pb and $\text{Li}_2\text{B}_4\text{O}_7$ matrix interferences are listed in Table 11 too.

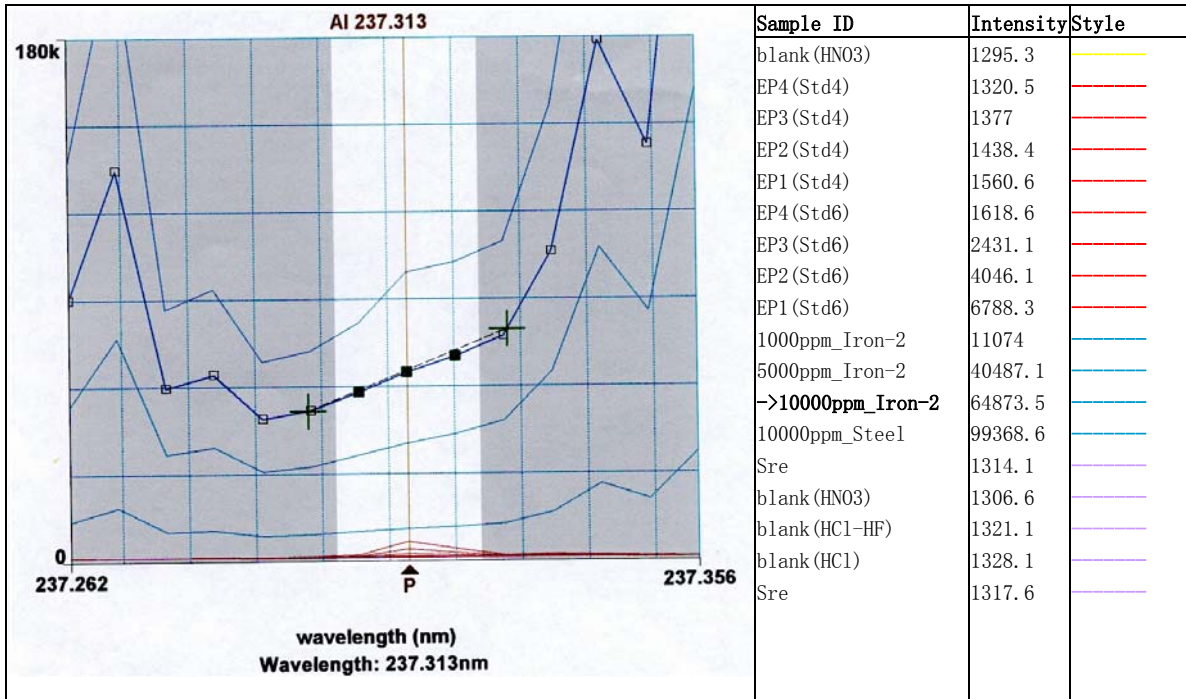


Fig.6 Spectra of Al at 237.313nm with the Fe matrix

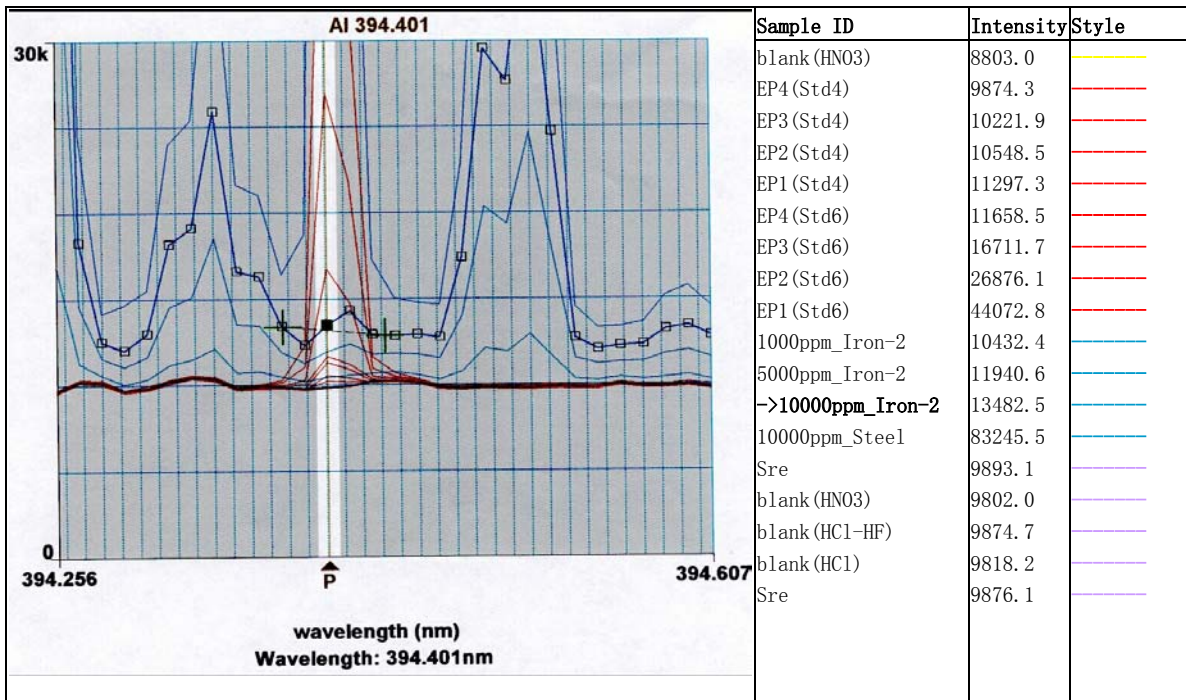


Fig.7 Spectra of Al at 394.401nm with the Fe matrix

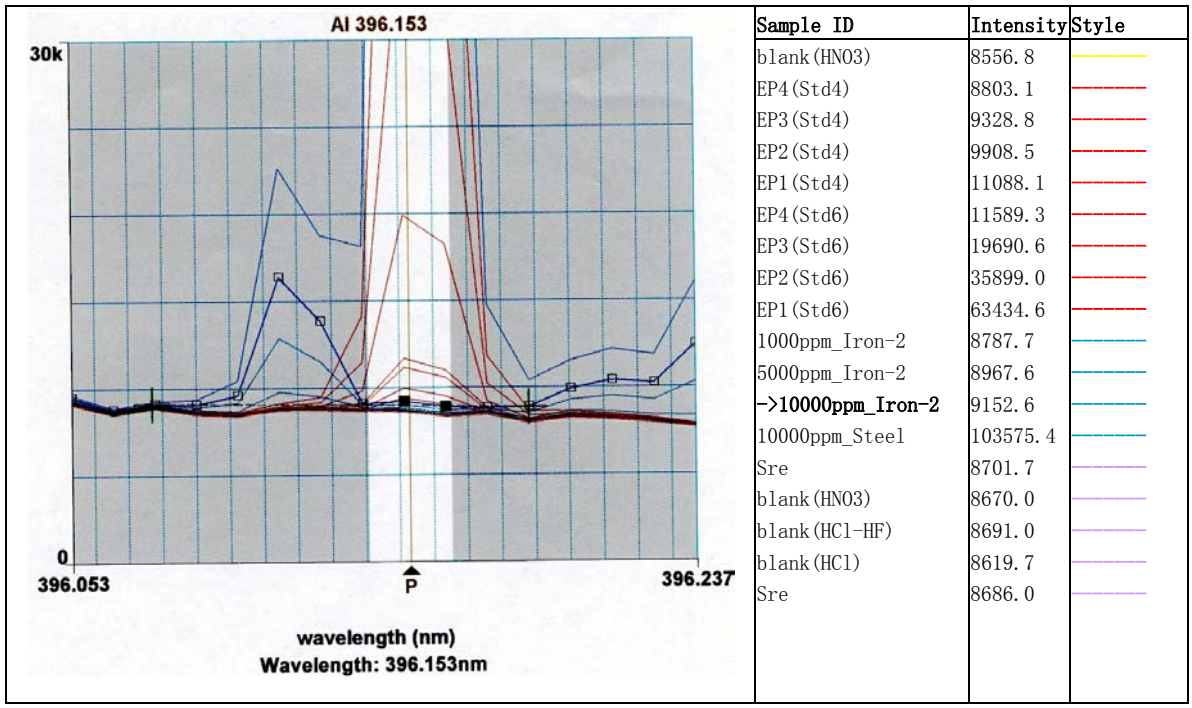


Fig.8 Spectra of Al at 396.153nm with the Fe matrix

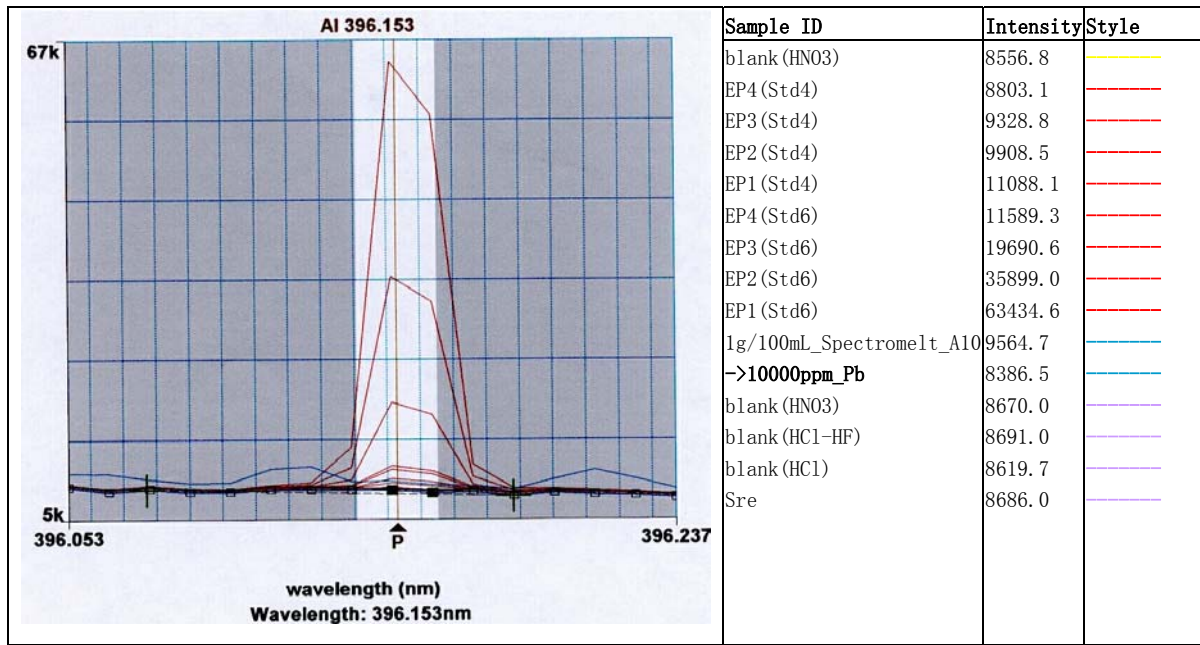


Fig.9 Spectra of Al at 396.153nm with the Li₂B₄O₇ (Spectromelt A10) and Pb matrix

Table 11 Interferences of Fe, Pb and Li₂B₄O₇ to 100 emission lines of 47elements

Element	Emission wavelength (nm)	Fe		Pb	Li ₂ B ₄ O ₇	Element	Emission wavelength (nm)	Fe		Pb	Li ₂ B ₄ O ₇
		left	right					left	right		
Ag	328.068	-	-	-	+	Ni	221.648	+	+	-	-
	338.289	-	+	-	-		231.604	-	-	-	-
Al	237.313	-	++	-	-	Os	225.585	+	+	-	-
	394.401	+	+	-	+		228.226	-	+	-	+
As	396.153	-	-	-	+	P	177.434	-	-	-	-
	188.979	-	-	-	+		178.221	+	+	+	+
Au	193.696	+	-	-	-	213.617	+	+	-	-	
	242.795	-	++	+	-	214.914	+	++	+	-	
B	267.595	+	+	-	-	Pb	217.000	++	+	-	-
	182.528	-	-	+	-		220.353	+	-	-	-
Ba	249.677	-	++	+	-	405.781	-	+	-	+	
	249.772	-	++	+	-	Pd	340.458	++	+	-	+
233.527	+	+	-	-	363.470		+	+	+	+	
Be	455.403	-	-	-	-	Pt	214.423	-	++	-	-
	313.042	-	-	-	-		265.945	+	+	+	+
Bi	313.107	-	-	-	-	Rb	780.023		+	-	-
	190.171	+	-	+	-		Re	197.248	-	++	++
Ca	222.821	++	-	+	-	204.908		+	+	++	-
	223.061	-	+	-	-	227.525	++	+	+	+	
Cd	315.887	-	+	-	+	Rh	233.477	++	+	-	-
	317.933	-	++	-	+		343.489	-	++	-	++
Co	393.366	-	+	-	+	Ru	240.272	++	-	+	+
	214.440	-	++	-	-		349.894	++	+	-	+
Cr	228.802	-	-	-	-	Sb	206.836	+	-	-	-
	228.616		++	+	-		217.582	++	+	++	-
Cu	238.892	+	+	++	-	231.146	++	-	-	+	
	205.560	++	-	-	-	Se	196.026	-	+	-	-
267.716	-	-	-	-	203.985		++	+	-	-	
Fe	221.459	+	-	+	+	Sn	189.927	-	++	+	+
	324.752	++	+	+	-		235.485		++	+	+
Ga	327.393			-	+	283.998	+	-	-	-	
	238.204			-	+	Sr	407.771	-	-	-	+
239.562			-	+	421.552		+	-	-	+	
Hf	259.939			+	+	Ta	226.230	+	-	-	-
	294.364	+	+	-	-		240.063	++	-	+	-
In	417.206	+	+	-	-	Te	214.281		+	-	-
	232.247	++	-	-	+		238.578	+	+	+	+
Ir	277.336	+	-	-	-	Ti	334.940	-	-	-	+
	303.936	+	+	-	-		336.121	++	-	+	+
K	325.609	++	+	-	-	Tl	190.801	+	-	+	-
	224.268	+	+	++	-		276.787	++	+	-	-
Li	766.490	-	-	-	-	V	290.880		++	-	-
	670.784	-	-	-	-		310.230		+	+	+
Mg	285.213	+	-	-	+	W	207.912	-	+	+	+
	257.610	-	-	++	-		224.876	-	++	+	+
Mn	259.372		++	-	+	Zn	206.200	-	-	++	-
	202.031	-	-	+	-		213.857		++	-	-
Na	203.845	-	+	-	-	Zr	339.197	-	++	+	-
	589.592	-	-	+	-		343.823	+	+	+	-
Nb	309.418	+	+	-	-						
	313.079	++	-	+	+						

+: spectral interference; ++: high spectral interference; -: no spectral interference

4. Suggestion on next steps

- Comparison of the LOD obtained by multielement solutions without matrix with the results of multielement analysis of high matrix solutions of 1000 µg/mL high pure Fe, Pb and Li₂B₄O₇ ;
- Elimination of matrix effects (matrix matching and internal standard calculation);
- Elimination of interferences by using multicomponent spectral fitting (MSF) method.