Technical Note: 40839

Pushing the boundaries of ICP performance with the iCAP 6000 Series - 66 Elements with detection limits less than 1µg/L

Key Words

- ICP
- iCAP 6000 Series
- Analytical performance
- Detection limits

Introduction

The first commercial ICP spectrometer from Thermo Scientific was introduced over 30 years ago. The iCAP Q (Jarrell Ash) and the ARL 34000 were simultaneous spectrometers based on spark spectrometers with the addition of a plasma source.

Towards the end of the 1970s, the first sequential ICP spectrometers appeared on the market. These instruments were able to scan any wavelength in the spectrum, thereby avoiding the restriction imposed by a fixed number of wavelength channels. However, analysis of large numbers of wavelengths was relatively slow due to the requirement to scan the spectrum.

In order to improve the speed of analysis without sacrificing wavelength flexibility, instruments with a combination of sequential and simultaneous spectrometers were developed. This gave rise in the early 1980s to elaborate spectrometers like the ARL 3580 and the Jarrel Ash Polyscan. These instruments were rather cumbersome and were still unable to conduct simultaneous measurements for background correction purposes.

The first completely simultaneous measurements of the entire wavelength spectrum became possible when the first IRIS "chip" spectrometers were introduced by Thermo Scientific in 1993. These instruments made use of a new Charge Injection Device solid state detector.

Since that time, this type (Advantage, Intrepid, Intrepid II) has evolved and is now capable of ten times the original analytical performance (detection limits, measurement quality etc.), coupled with enhanced productivity.

The advanced design of the Thermo Scientific iCAP 6000 Series

To achieve further progress in the development of new ICP spectrometers, a thorough analysis was carried out into the needs of customers, instrument manufacturers and technical after-sales service. Customer-related issues concerning performance, sensitivity, analysis speed, sampling rate, ease of use, operating costs and enhanced functionality were also evaluated. Thermo Scientific strives to achieve a robust design, reduced assembly time, reduced calibration and test time, improved performance specification and reliability targets, as well as reduced installation times and associated costs.

These requirements called for advanced design and production techniques to support a novel design concept. For the Thermo Scientific iCAP 6000 Series, modelling techniques that are normally associated with the design of aircraft and motor vehicles were employed. As large temperature differentials occur inside an ICP spectrometer, it is important to investigate how the heat dissipation is handled. Temperatures inside a plasma can be as high as 10,000 °C, while the optical tank needs to be maintained at an absolutely stable 38 °C and the detector needs to be cooled to -45 °C. Any heat transfer between these components would seriously degrade the performance of the instrument during operation. Maintaining a stable environment has been achieved in the iCAP by using a managed air flow through the base casting of the instrument, which maintains a thermal break between the polychromator and the torch box.

The optical components are required to provide a high quality image with efficient energy transfer, good optical resolution and low background signals. Small amounts of water vapour or oxygen in the optical path will seriously attenuate signals for wavelengths <190 nm. Consequently it is necessary to purge the optical tank with an inert gas such as nitrogen or argon. To minimize operating costs the gas flow rates should be as low as possible. The iCAP uses just 1 L/min purge gas in standby mode, and only an additional 2 L/min when in use.

The outcome of this development is an ICP spectrometer which differs in terms of performance and design from any other instrument. In the Thermo Scientific iCAP 6000 Series, the following components have been thoroughly optimized and implemented:

- Robust instrument optics based on 3 castings
- Ergonomic design
- Optical system with aspherical concave and convex mirrors
- High-performance detector with CID86 chip
- Compact solid state generator
- Torch design

The spectrometers have a footprint measuring 84 cm in width and are 74 cm in depth. The height without extraction flue is approx. 50 cm. Weighing just 85 kg, these units are easy to transport and require a minimum of bench space in the lab.

Figure 1: View of the iCAP 6500 with a Cetac autosampler

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Analytical performance of the spectrometer series

The iCAP 6000 Series platform comprises of the Thermo Scientific iCAP 6300 and the Thermo Scientific iCAP 6500. They have identical optical designs but different gas control, and measurement modes. The iCAP 6500 also has the ability to measure transient signals and has enhanced software features and range of accessories. Both instruments are available with a Duo plasma source (axial/radial) or a dedicated Radial view plasma.

The sample introduction assembly has been greatly simplified. The semi-demountable torch design has twist lock couplings to enable the torch and/or injector tube to be replaced rapidly. In addition, all gas supplies are auto-connecting. An improvement to the torch design has resulted in our Enhanced Matrix Tolerance (EMT) torch which offers significant improvements in the long-term signal stability of the instrument when highly concentrated sample matrices or organic solvent matrices are being analyzed. Spray chamber connection is simplified by the use of precision ground ball and socket joints.

The analytical performance of the iCAP 6000 Series is demonstrated by its exceptional detection limits, enhanced linearity, superior long-term stability and high resolution images. This capability is based largely on the design of the Echelle optical system and the properties of the new CID86 camera. Figure 2 shows an Echellogram for the phosphorus 177.498 nm wavelength. The peak is clearly defined with excellent resolution and no tailing into the baseline indicating sharp focus of the image on the detector surface.

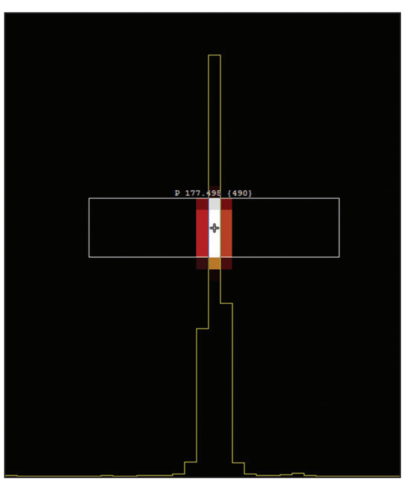

Figure 2: Image of P 177.498 nm on the CID86 detector

The sharpness of image shown in this illustration is achieved right across the detector surface. This means that the maximum radiation intensity of emission lines from the plasma can be detected by the CID detector. Together with the effective sample introduction system, this gives detection limits for a range of elements which have never been achieved before on any other ICP spectrometer.

Table 1 provides a summary of the detection limits for most elements that can be determined by ICP. These detection limits were determined using the blank value method using 10 separate measurements of the blank. Optimum plasma conditions were used and calculated 3x the standard deviation of the 10 replicate measurements. The results for the best lines on different elements are presented in Table 1 and are assigned to concentration ranges arranged in a logarithmic progression. For example, 10 elements yield detection limits below 0.01 µg/L, such as Mg 279.553 nm with 0.0023 µg/L. The remaining elements are arranged accordingly.

Detection Limit range in µg/L	Number of elements	Elements
≤ 0.01	10	Ba, Be, Ca, Eu, Li, Lu, Mg, Sc, Sr, Yb
> 0.01 and ≤ 0.1	17	Ag, Al, Cd, Cr, Dy, Er, Hg, Ho, K, La, Mn, Na, Ti, Tm, Y, Zn, Zr
> 0.1 and ≤ 1	39	Mo, Fe, V, Ni, Re, Co, Tb, Nd, Gd, B, Sm, Nb, Cu, W, Au, Hf, Ru, Ce, Rb, Pr, Sn, Tl, Pd, P, Pb, Th, Ga, Te, Ir, Os, Pt, Ta, Se, Rh, Sb, As, U, Si, Bi

Table 1: Overview of detection limits (in µg/L) for ICP elements (blank value method; 3σ criterion)

This list includes elements whose lines lie in the higher wavelength region, e.g. sodium or potassium which have very low detection limits of 0.03 or 0.1 µg/L. This can be attributed to the high signal-background ratio in this range. The excellent UV performance capability of the optical system is demonstrated very effectively with Al 167.079 nm or Pb 168.215 nm with their respective detection limits of 0.03 µg/L and 3 µg/L.

Table 2 illustrates measurements for detection limits and stability. Lines with high and low excitation energy levels are measured using a common method. A calibration was performed using a blank and a 50 µg/L standard. The detection limit was then determined after which the calibration standard was measured back after 2 and 4 hours. This demonstrated that, even in a multi-element method including a diverse range of elements, the detection limits described above can be achieved. At the same time, this illustrates the high stability of the optical and sample introduction systems. Although multiple analyses of aqueous based samples and acid digests were carried out between the repeat measurements of the standard, no unacceptable deviations from nominal values were observed even after four hours.

Element	Unit	Detection Limit	Calibration		After 2 hours Hrs.: 1st back measurement		After 4 hours Hrs.: 2nd back measurement	
			Average	*RSD %*	Average	*RSD %*	Average	*RSD %*
Al 167.079 nm	µg/L	0.042	50.0	2.5	50.8	0.4	52.2	0.5
As 189.042 nm	µg/L	0.96	50.0	2.7	50.6	0.7	50.3	0.3
B 249.773 nm	µg/L	0.43	50.0	1.5	52.5	4.8	51.4	0.1
Cd 214.438 nm	µg/L	0.023	50.0	1.6	49.9	1.2	49.7	0.7
Cr 205.552 nm	µg/L	0.079	50.0	1.7	51.0	0.5	51.0	0.3
Cu 324.754 nm	µg/L	0.14	50.0	0.5	46.5	15.2	51.4	0.4
K 766.490 nm	µg/L	0.11	50.0	0.2	49.9	11.0	49.9	0.4
Mo 202.030 nm	µg/L	0.12	50.0	1.4	50.1	0.4	50.5	0.2
Na 589.592 nm	µg/L	0.021	50.0	0.4	50.5	5.0	51.9	0.8
Ni 231.604 nm	µg/L	0.11	50.0	1.6	50.3	0.6	50.6	0.1
Pb 220.353 nm	µg/L	0.43	50.0	1.8	50.3	0.9	50.7	0.1
Sb 206.833 nm	µg/L	0.46	50.0	1.7	48.6	2.2	50.0	0.3
Sn 189.989 nm	µg/L	0.26	50.0	2.4	49.0	0.5	48.7	0.0
Ti 190.820 nm	µg/L	0.28	50.0	2.0	49.3	1.0	50.6	0.2
Zn 202.548 nm	µg/L	0.041	50.0	2.0	50.5	2.0	50.2	0.9

Table 2: Investigation of elements at trace concentrations: Detection limits and stability after 2 and 4 hours

Measurements of low concentrations are just one requirement of ICP spectrometry. More often, spectrometry involves the demanding task of measuring relatively high concentrations. For example, the presence of alkali and alkali earth metals may need to be accurately determined in water samples. For this task, a precisely linear calibration curve is required. Figure 3 below shows the broad linear range for the K 769.896 nm emission line using the iCAP 6500 Duo system in radial viewing mode.

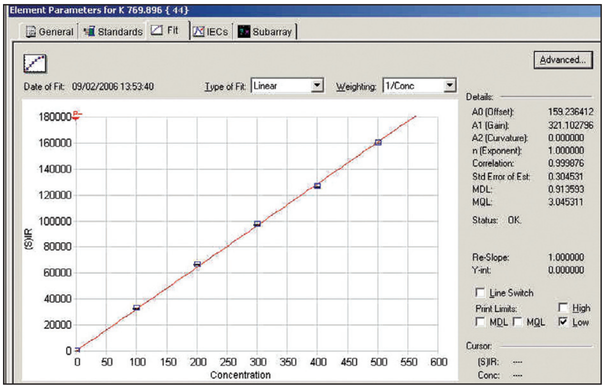

Figure 3: Calibration line of potassium (K 769.896 nm), from 0 to 500 mg/L (radial measurement with the iCAP 6500 Duo)

The wide dynamic range of the CID86 of 10^7 enables a wide linearity range for emission lines which, depending on the line involved, can amount to between 4.5 and 5.5 orders of magnitude of concentration (starting from the detection limit). Table 3 shows the linearity ranges of selected lines which relate to environmental analyses.

Line	Linearity range mg/L axial	Radial
Al 167.079 nm	2	20
Al 396.152 nm	40	500
Al 309.271 nm	100	1000
Ca 373.690 nm		1000
Fe 271.441 nm		1000
Fe 371.994 nm		2500
K 766.490 nm		500
K 769.896 nm		1000
Cd 214.438 nm	5	
Cd 361.051 nm	200	
Zn 206.200 nm	15	
Zn 334.502 nm	150	

Table 3: Linearity ranges of selected lines in axial and radial plasma examinations performed with the iCAP 6000 Duo

The high level of sensitivity, and the ability to measure high concentrations, is very significant for real analytical tasks. These properties are illustrated very well for the analysis of trace elements and major consituents in water samples. Table 4 shows the analysis results for a range of reference materials obtained with the iCAP 6500 Duo. The data demonstrates excellent agreement with certified values.

Line	Unit	SW-1		6019 River Thames		6017 Rainwater		TMRAIN-95	
		Measured value	Reference	Measured value	Reference	Measured value	Reference	Measured value	Reference
Ca 318.128 nm	mg/L	2.02	2.00	113	109	3.53	3.50	0.66	0.66
Mg 279.806 nm	mg/L	0.39	0.40	4.46	4.62	0.40	0.40	0.168	0.170
Na 589.592 nm	mg/L	1.94	2.00	25.5	24.7	4.5	4.3		
K 766.490 nm	mg/L	0.204	0.200	4.88	4.78	0.79	0.75		
Fe 259.940 nm	µg/L	19.8	20	267	273	18.6	18.0	24.3	24.1
Al 167.079 nm	µg/L	50.5	50.0	69	73	8.8		1.8	1.7
Cd 214.438 nm	µg/L	0.50	0.50	0.11	0.11	0.11	0.13	0.47	0.48
Cr 267.716 nm	µg/L	2.0	2.0					0.80	0.79
Cu 324.754 nm	µg/L	19.5	20	15.3	15.4	16.3	16.1	6.4	6.2
Mn 257.610 nm	µg/L	9.8	10	23.2	0	11.5	11.8	6.1	6.1
Ni 231.604 nm	µg/L	10	10	3.1	2.6	1.5	1.6	0.7	0.8
Pb 220.353 nm	µg/L	5.5	5.0	5.6	5.2	1.1	1.0	< 0.5	0.29
Zn 213.856 nm	µg/L	21.3	20	60	59.7	123.6	126.5	16.6	11.1

Table 4: Analysis results for various different reference materials, compared to the certificate

Summary

The iCAP 6000 Series of ICP emission spectrometers have proven themselves to be exceptional as a high performance instruments for both routine laboratories seeking the ultimate in detection capability and those with varying and demanding analytical needs. Over 1000 global customers rely upon the iCAP 6000 to deliver the very best performance in their laboratories, day after day.

The excellent stability of the Echelle optical unit, the new solid state, swing frequency semiconductor radio frequency plasma generator and the optimized CID86 camera deliver unique opportunities for ICP spectrometry and provide the analyst with the highest standards of precision and the lowest detection limits currently available, with detection limits for 66 elements at levels less than 1 µg/L.

The wide dynamic range of the detector, coupled with the radial view of the Duo, are ideal for precision measurements, even at high concentrations.

Alongside analytical performance, commercial considerations also play an important role in the selection of an ICP instrument. The entire iCAP 6000 concept delivers dramatic progress in terms of sample throughput and operating costs. Extremely short installation and stabilisation times are achieved through the compact configuration of the entire structure. Stability, high transmission optics and flexible software enable short measurement times and reduced operating costs.

In addition to these offices, Thermo Fisher Scientific maintains a network of representative organizations throughout the world.

Africa
+43 1 333 5034 127
Australia
+61 2 8844 9500
Austria
+43 1 333 50340
Belgium
+32 2 482 30 30
Canada
+1 800 530 8447
China
+86 10 8419 3588
Denmark
+45 70 23 62 60
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+43 1 333 5034 127
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+31 76 579 55 55
South Africa
+27 11 570 1840
Spain
+34 914 845 965
Sweden/Norway/Finland
+46 8 556 468 00
Switzerland
+41 61 48784 00
UK
+44 1442 233555
USA
+1 800 532 4752

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