Wide Applicability of ICP-OES Analyses in the Metallurgical Industry

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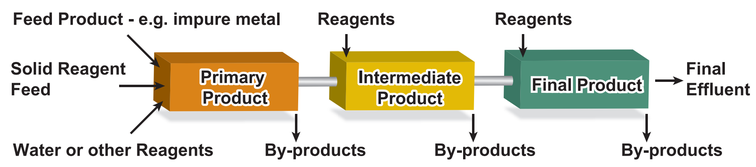
Overview

The modern metallurgical industry requires a large array of analysis sample types to function correctly and efficiently, with minimum environmental risk and complying with local regulations. The sample types will ordinarily include feed or reagents, intermediate and final products. In addition, other sample analyses will be required from cooling systems, waste products, by-products and final residues or effluents. All of these sample types require a versatile instrument with a wide range of applicability to the Metallurgical Industry and its samples. This presentation will show that ICP-OES analysis can be successfully utilised for all of the general sample types occurring in the metallurgical industry.

Typical Metallurgical Sample Types

FIGURE 1. A generic metallurgical process.



Typical Sample Types and Examples

1. Feed Reagents	2. By-products
• Water/liquids e.g. acid reagents, cyanide solution • Solid feed reagents e.g. fluxes, slags, chemicals	• Waste salts • Effluents
3. Feed Products	**4. Primary, Intermediate and Final Products**
• Raw ore for metals extraction and purification • Metal process by-products e.g. metal salts, concentrated mixed base metal or precious metals products • Impure metals e.g. blister copper, iron ingots • Pure metals for pure alloy manufacture	• Metals in various forms and purities • Solid metal sampling

1. Feed Reagents and 2. Waste salts and Effluents

Feed reagents, water and effluents analyses are frequently controlled by local legislation. Metallurgical plants often augment these legislative analyses with their own regiment of sample analysis – frequently to minimise costs by reducing valuable material loss and possible over-consumption of reagents. Typical analyses may include trace elemental analysis on the following:

- Feed water for elements detrimental to the plant process
- Feed chemicals and reagents for foreign contaminants
- Effluents for heavy elements detrimental to the environment

Analyses of these types in a metallurgical environment typically look for low-level trace elements in low to high total dissolved solid environments. Matrices may vary from mg/L level to g/L level while traces may go as low as µg/L in concentration. The typical ICP-OES instrument may find the above requirements problematic but recent advances in ICP-OES instruments, especially the more sensitive axial view (Duo), have improved the detection limit capabilities to such an extent that other, more sensitive instrumentation is often not required.

The example in Figures 2 and Table 1 utilises EPA method 3050B for dissolution and EPA Method 6010B for analysis of ground waters, industrial wastes and sludges. Table 2 shows the detection limits and linear ranges for EPA 200.7. The detail in these application notes show that the Thermo Scientific iCAP 6000 Series Duo used for the analyses far exceeds the requirements of the EPA protocols. Note the excellent method detection limits achieved in these methods.

FIGURE 2. EPA 6010B Method Application Note using Thermo Scientific iCAP 6500 Duo.

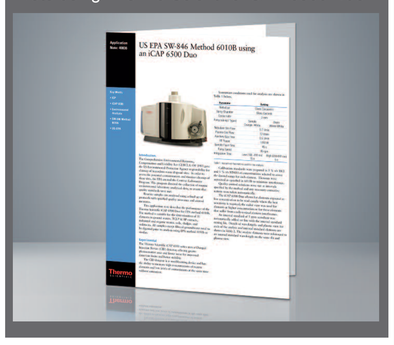


TABLE 1. Method detection limits for EPA 6010B note using Thermo Scientific iCAP 6500 Duo.

Element	Wavelength (nm)	Plasma View	MDL (ppb)
Ag	328.068	Axial	0.88
Al	308.215	Radial	22
As	189.042	Axial	1.6
Ba	455.403	Radial	0.39
Be	313.107	Radial	0.29
Ca	315.887	Radial	6.6
Cd	214.438	Axial	0.051
Co	228.616	Axial	0.26
Cr	267.716	Axial	0.39
Cu	324.754	Axial	0.45
Fe	271.441	Radial	73
K	766.490	Radial	40
Mg	279.079	Radial	37
Mn	260.569	Radial	0.17
Na	589.592	Radial	9.3
Ni	231.604	Axial	0.31
Pb	220.353	Axial	0.76
Sb	206.833	Axial	1.2
Se	196.090	Axial	1.9
Tl	190.856	Axial	0.66
V	292.402	Axial	0.39
Zn	206.200	Axial	0.20

TABLE 2. Method detection limits and linear ranges for EPA 200.7 note using the Thermo Scientific iCAP 6500 Duo.

Analyte	View*	LDR (mg/L)	Achievable 3-s IDL with blank**	Robust 3.14-s MDL with MDL solution	Drinking Water Level of Interest
Ag3280	R	> 2	4 (0.7)	10	100
Al3082	R	> 200	40 (5)	100	50-200
As1890	A	> 50	2	4	10
As1937	A	> 50	2	4	10
B_2496	R	> 50	6 (1)	10	–
Ba4934	R	> 50	1.5	3	2000
Be3130	R	> 50	0.2 (0.03)	1	4
Be3131	R	> 50	0.3 (0.05)	4	4
Ca3158	R	> 500	8 (1)	20	–
Cd2265	A	> 50	0.1	0.2	5
Cd2288	A	> 50	0.1	0.2	5
Co2286	A	> 50	0.3	0.5	–
Cr2055	A	> 50	0.1	0.2	100
Cu3247	R	> 50	3 (0.5)	4	1000
Fe2599	R	> 300	2 (0.3)	3	300
Hg1849	A	> 2	0.5	2	2
Hg1942	A	> 2	0.5	1	2
K_7664	R	> 200	40 (5)	100	–
Li6707	R	> 50	1 (0.1)	2	–
Mg2795	R	> 50	0.05 (0.008)	0.1	–
Mn2576	R	> 50	0.5 (0.08)	0.8	50
Mo2020	A	> 50	0.3	0.5	–
Mo2038	A	> 50	0.5	1	–
Na5889	R	> 200	20 (3)	70	–
Ni2216	A	> 50	0.1	0.2	–
Ni2316	A	> 50	0.3	0.5	–
P_1774	A	> 50	1	2	–
P_2149	A	> 50	2	6	–
Pb2203	A	> 50	1	2	15
S_1820	A	> 50	2	10	250,000
Sb2068	A	> 50	1	4	6
Se1960	A	> 50	2	4	50
Si2516	R	> 50	8 (1)	20	–
Sn1899	A	> 50	0.4	2	–
Sr4077	R	> 50	0.07 (0.01)	0.2	–
Sr4215	R	> 50	0.2 (0.02)	0.4	–
Ti3349	R	> 50	2 (0.3)	4	–
Ti3349	R	> 50	2 (0.3)	3	–
Tl1908	A	> 50	1	2	2
V_2924	R	> 50	3 (0.5)	6	–
Zn2138	A	> 50	0.2	0.6	5000

*R = Radial, A = Axial
** Bracketed figures show axial view values for radially viewed elements

3. Feed Products

Feed product samples ordinarily include all of those materials that contain the economic elements for the primary, intermediate and final product types. To reduce process costs, the feed materials may contain medium to high levels of economic materials and undesirable elements which must be removed in the process. Typical analyses may include trace to percentage level analyses on the following:

- Low-concentration ores, intermediate products or even final products from a pre-concentration process
- By-products from another process e.g. metal salts
- Alloy production feeds

Accurate analysis in the presence of high concentrations and interferences is essential, both from a metal accounting perspective and efficient process control.In this type of analysis, spectral and matrix interferences must be removed. In many cases, spectral interferences can be avoided completely if the instrument has full spectrum coverage. Matrix interference requires a robust plasma and RF generator, plasma optimisation and preferably a sensitive dedicated radial instrument.

The example in Figures 3, 4 and Table 3 show an analysis of medium grade (0.06 - 0.14%) precious metal sulphides in the presence of high concentrations of base metals (0.3 - 48%). The iCAP 6000 Series high resolution radial instrument chosen for the analysis did not require any other precautions against interferences other than a judicious choice of lines and minor optimisations of plasma conditions. The linearity in this base metal environment was shown to be excellent, as did the correlations between found and expected concentrations. The linearity, accuracy and ease of use are in part due to advances in solid-state generators and high stability optics.

FIGURE 4. Linear Pt 500 ppm range in high base metal matrices.

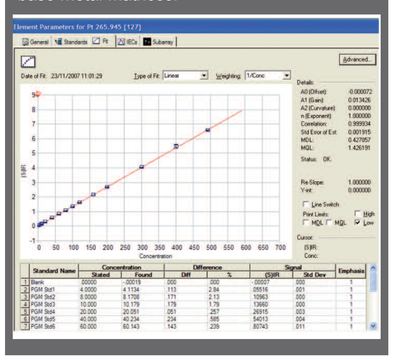


FIGURE 3. Accurate precious metal sulphide analysis.

TABLE 3. Excellent recoveries in the presence of high base metal matrices.

Element	Aliquot 1 (ppm)	Aliquot 2 (ppm)	Aliquot 3 (ppm)	Average ppm	Expected ppm (± 2sd)
Au 267.595 nm	67.0	70.6	70.0	69.2	67.9 ± 1.7
Pd 340.458 nm	784	813	849	815	817 ± 26
Pt 265.945 nm	1250	1383	1283	1305	1305 ± 44
Rh 343.489 nm	186	197	203	195	193 ± 8
Ru 267.876 nm	475	513	520	503	489 ± 18

4. Primary, Intermediate and Final Products

Metallurgy products, from whatever part of the process, may be presented in a multitude of forms and different phases - liquid or solid; powder, solid metal and alloys.

Typical analyses may involve:

- Trace, minor, major elements;
- Metal accounting in liquid and solid phases.

The analyses are commonly performed after sample dissolution but if dissolution is difficult or inaccurate, may also involve solid sampling techniques. The examples shown below are from final products of a pure metals and alloys manufacturer and a precious metal refinery. Table 4, Figure 5 and 6 show the analysis of impurities in pure tungsten after dissolution.

TABLE 4. Impurities in pure tungsten.

Element	Sample 1 (ppm in solid)		Sample 2 (ppm in solid)		Method DL (ppm in solid)
	Measured	Expected	Measured	Expected	
K 766.490 nm	90.3	90.5	27.1	32	8.7
Si 251.611 nm	202	228	ND	–	11.4

FIGURE 5. Impurities in pure tungsten.

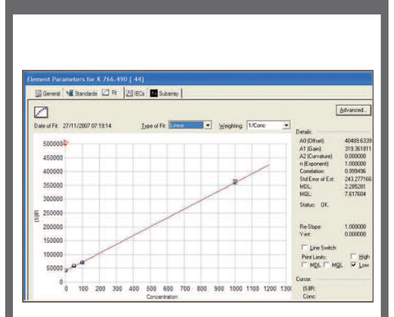


FIGURE 6. Potassium 766.490 nm subarray showing blank, standards and samples.

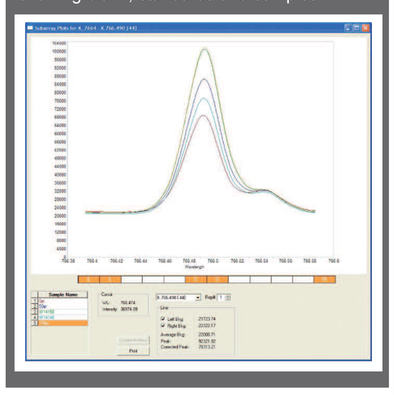


Table 5, Figures 7 and 8 show the solid metal analysis of impurities and silver content in pure silver by solid-sampling spark ablation – silver is determined by the concentration-ratio technique and the impurities in concentration mode. Both analyses use iCAP 6000 Series Duo instruments.

TABLE 5. Results of a typical analysis with duplicates (1472-2, 1472-2') and detection limits (all units in % w/w).

	302	1247	1472-2	1472-2'	Detection Limit
Ag	99.999	99.940	99.881	99.884	
As	< DL	0.00007	0.00007	0.00007	0.00005
Au	0.00006	0.0069	0.0100	0.0098	0.00002
Bi	< DL	0.0056	0.0045	0.0044	0.00005
Cd	< DL	0.000003	< DL	< DL	0.000003
Co	0.000019	0.00025	0.000047	0.000045	0.000003
Cr	0.000025	0.00013	0.00001	0.00001	0.00001
Cu	0.00017	0.0315	0.0945	0.0931	0.00001
Fe	0.00015	0.00069	0.00008	0.00007	0.00003
Mn	0.00017	0.00003	0.000006	0.000004	0.000003
Ni	< DL	< DL	0.00001	0.00001	0.00001
Pb	0.00037	0.00073	0.00027	0.00028	0.00005
Pd	< DL	0.0017	0.00176	0.00171	0.00003
Pt	< DL	0.0019	0.00188	0.00184	0.00005
Rh	< DL	0.0026	0.00255	0.00250	0.00003
Sb	< DL	0.00064	0.00020	0.00020	0.00003
Se	0.00010	0.00095	< DL	< DL	0.00005
Sn	< DL	< DL	< DL	< DL	0.00003
Te	0.00006	0.0047	0.00176	0.00175	0.00005
Ti	< DL	< DL	0.00016	0.00018	0.00003
Zn	0.000017	0.00009	0.00013	0.00015	0.000005

FIGURE 7. Pd 340.458 nm calibration.

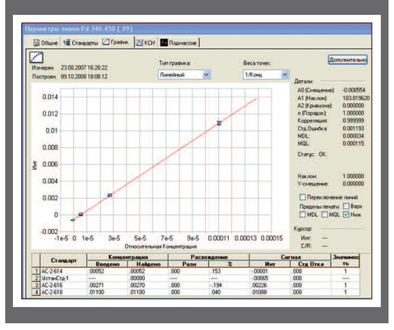
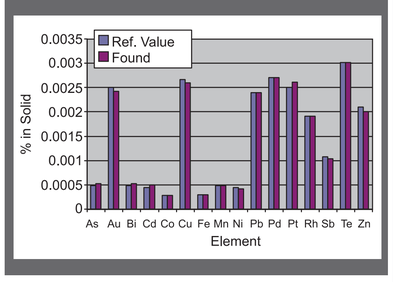


FIGURE 8. Comparison of found and reference values - Kolyma silver impurities vs CRM AC-2-646.



Conclusions

ICP-OES has been considered a “mature” technique and a routine workhorse in the metallurgical industry for a number of years. However, the development of, and investment in, ICP-OES is continual and in recent years detection limits, solid-state generators, optical systems, ease-of-use and cost of ownership have all improved well beyond the expectations of the scientific community. The sheer versatility of the ICP-OES technique is well-demonstrated by the above analyses of traces in waste and water samples at ppb and sub-ppb level to the analysis of high-grade solid silver at % level – and any number of analysis types in-between.

In short, no metallurgical laboratory should be without a modern, simultaneous ICP-OES like the Thermo Scientific iCAP 6000 Series.