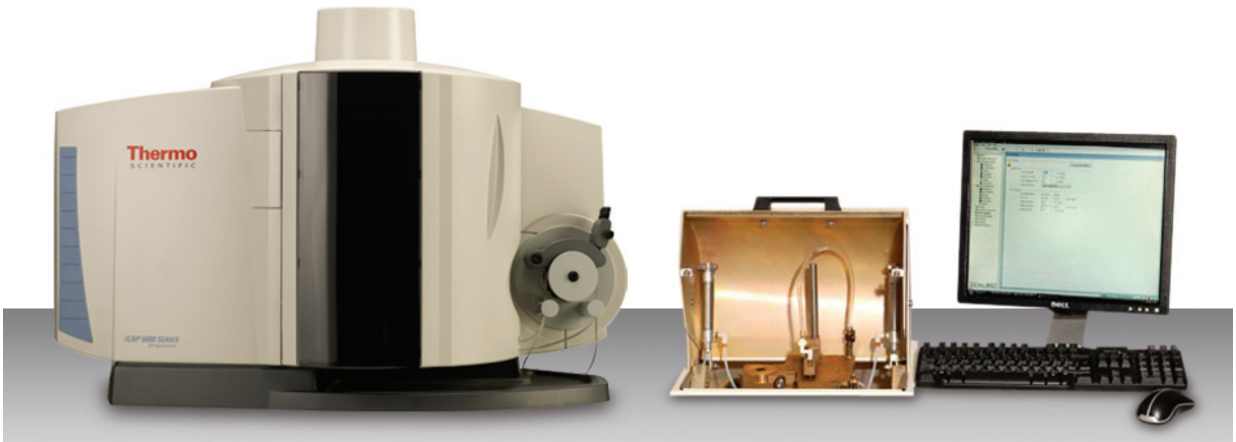
Application Note: 40984

Rapid Analysis of Impurities in Silver using a Separate Sampling and Excitation Accessory (SSEA) and Thermo Scientific iCAP 6500 Duo

G. Buchbinder and N. Verblyudov, Intertech Corporation, Novosibirsk Office, Russia and
A. Clavering, Applications Specialist ICP, Thermo Scientific, Cambridge, UK

Key Words

- Solid Sampling
- Rapid Analysis
- Metallurgy
- Precious Metals
- SSEA
- iCAP 6500 Duo



Benefits:

- Rapid, bulk analysis
- Minimal sample preparation
- Versatility – solids and liquid sampling
- Measurement of sample as is – no loss of elements in sample preparation
- Unique combination of instrumentation

Introduction

Silver is one of the oldest metals known to humanity and is a precious metal which is still very important in minting, jewelry and industry.

The maximum concentration of impurities allowed in saleable silver bullion is at ppm and sub-ppm levels in solid and therefore requires extensive purification and sensitive analyses. Silver refinery plants receive the low assay silver from suppliers and have to analyse the silver, gold and Platinum Group Metals (PGM) content as well as toxic and harmful elements which interfere with the refinery process. These impurity levels must be carefully monitored throughout the refining plant to prevent metal and cost losses in the plant resulting from the need to reprocess contaminated products. Atomic spectroscopy is the preferred method to analyse pure silver, as opposed to other techniques, due to the relatively low spectral emissions from the silver matrix.

ICP spectrometry is a standard method for analysis of silver, particularly in Russia and the other successor states of the former USSR. Silver may be analyzed after the metal dissolution in diluted nitric acid (1:1), but several significant problems exist. Gold and Rhodium are not soluble in nitric acid and require a subsequent aqua regia treatment, possibly after filtration. If the sample is not filtered and the whole sample is subjected to the aqua regia, a lengthy precipitation separation of the silver is often required. The silver needs to be separated before the aqua regia treatment since silver has limited solubility in hydrochloric acid. In addition, this precipitation procedure can produce errors in the impurity analysis by co-precipitating portions of the analyte traces.

SSEA (Separate Sampling and Excitation Accessory) is an instrumental solution for the procedural problems mentioned above. The Refineries and Mints in Russia, Ukraine, Kazakhstan, Uzbekistan and Kyrgyzstan use the iCAP 6000 Series and its predecessors, the ICAP 61 and IRIS ICPs, with SSEA for the analysis of gold. The ICP-SSEA method will also be included in a forthcoming version of Russian State Standard (GOST) for Analysis of Gold. The refineries above and other precious metal manufacturers have found that the SSEA gives them a rapid analysis with minimal sample preparation making it ideal for plant control – sample preparation and analysis within 20 minutes is typical.

Kolyma State Refinery, in the Magadan region of Russia, purchased a Thermo Scientific iCAP 6500 Duo with SSEA (Figure 1) to replace their DC Arc Atomcomp 2000 for the analysis of silver.

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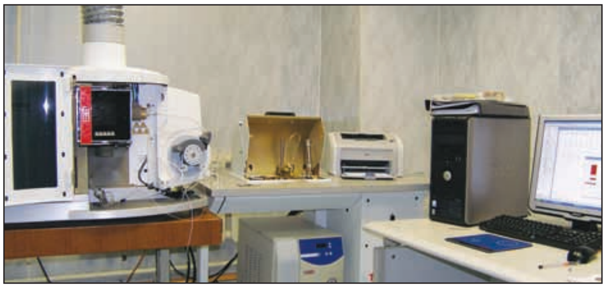


Figure 1: iCAP 6500 Duo attached to the SSEA in Kolyma Refinery

This application note describes the use of, and presents data from, the technique used by the Kolyma Refinery for the impurity analysis of high and low grade silver.

Principle

The SSEA utilizes a high voltage spark to ablate a metal or conductive sample, producing a dry aerosol. The aerosol is transferred to the plasma using the iCAP's main gas supply at a reduced pressure. The metal or sample vapour now undergoes the same processes of excitation and emission as a liquid sample. Only a small part of the sample is ablated and the sample can be used repeatedly until the surface is covered with spark sites. The sample then simply requires a repeat of the initial surface preparation and skimming before reuse.

Any metal sample including steels, platinum group metals, gold and other conductive materials can be sampled with the ablative process. This rapid, efficient and easy to use process is ideal for the direct analysis of noble metals and other conductive substances by ICP, provided that the detector used can analyze trace intensities among the high background signals. The iCAP 6500 uses a CID camera which, unlike CCD cameras, is bloom-resistant and can analyze for trace elements in the presence of high intensity emissions whilst allowing for full wavelength coverage. The complex spectral matrices produced by solid metal sampling make full wavelength coverage and a high resolution optical ICP such as the iCAP 6500, essential. The full wavelength coverage allows maximum choice of alternate wavelengths to reduce interferences and the high resolution makes those interferences less likely.

Instrumentation

The award winning Thermo Scientific iCAP 6500 Duo spectrometer was chosen due to enhanced sensitivity in axial view and the ability to couple with, and fully support, a conductive metal spark accessory like the SSEA. The SSEA requires the enhanced capabilities of the iCAP 6500 to enable the advanced features of electronic control and triggering - no other model of ICP is capable of these features.

Parameters of ICP

Parameter	Setting
Centre Tube	2 mm
Torch Orientation	Duo
RF forward power	1150 W
Coolant gas flow	12 L/min
Auxiliary gas flow	0.5 L/min
Integration Time	15 seconds

Parameters of SSEA

Parameter	Setting
Power Level	3
Frequency	500 Hz
Pressure in Delivery Line	18 psi

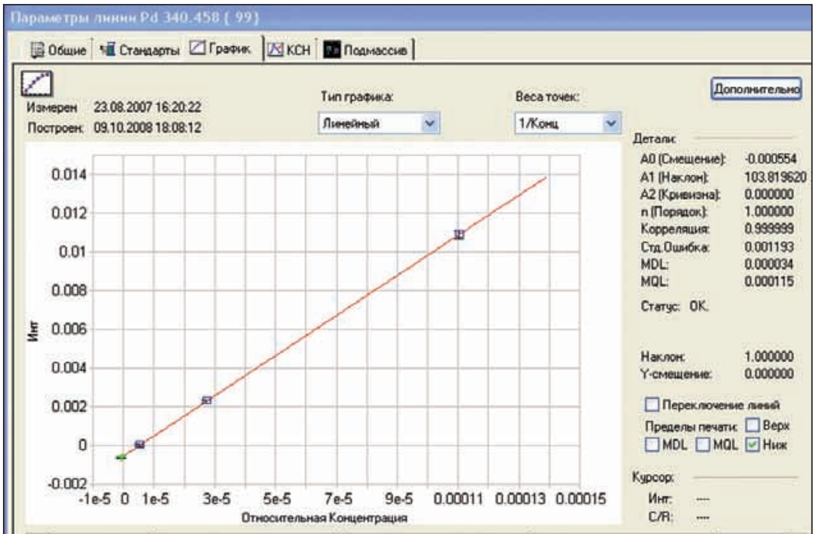
Elements and lines that are used for this method at the Kolymar Refinery are displayed in Table 1.

Element	Wavelength, nm	Element	Wavelength, nm
As	189.042	Pb	220.353
Au	242.795 267.595	Pd	340.458
Bi	190.241	Pt	214.423
Cd	226.502	Rh	343.489
Co	228.616	Sb	217.581
Cr	267.716	Se	196.090
Cu	327.396	Sn	189.989
Fe	259.940	Te	214.281
Mn	257.610	Ti	336.121
Ni	221.647	Zn	213.856

Table 1: Element and line selection for silver analysis by SSEA and iCAP 6500 Duo

The calibration standards used were acquired from a library of Russian State Reference Samples of silver. The concentration values of the standards are certified as percentage concentration and were used as a direct calibration values. The silver wavelengths at 232.468 nm and 233.137 nm were used as internal standard lines to maximize the precision of the method and minimize the effect of transport efficiencies.

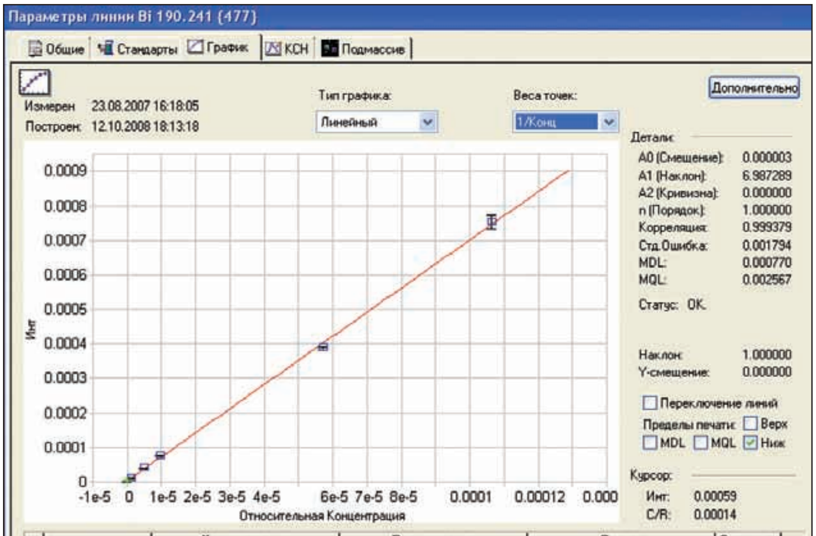
Calibration graphs (Graphs 1 and 2 below) with excellent correlation coefficients were generated by this method. All the data shows an exceptionally accurate and stable analysis.



	Стандарт	Концентрация		Расхождение		Сигнал		Значимость
		Введено	Найдено	Разн	%	Инт	Стд Откл	
1	AC-2-614	.00052	.00052	.000	.153	-.00001	.000	1
2	УстанСтд-1	-----	.00000	-----	-----	-.00065	.000	-----
3	AC-2-616	.00271	.00270	.000	-.194	.00226	.000	1
4	AC-2-618	.01100	.01100	.000	.040	.01088	.000	1

Graph 1: Pd 340.458 nm calibration

Liquid samples of reference materials can be used to build a calibration. Liquid calibration standards CH-4 and CH-7 are shown in Graph 2 below; the other standards are solids. The liquid standards can be used in conjunction with solid samples using a purpose-designed twin inlet spraychamber. The use of a liquid calibration requires that a conversion factor be established between the liquid and solid sample responses, and is useful in cases where suitable solid standards are not readily available.



	Стандарт	Концентрация		Расхождение		Сигнал		Значимость
		Введено	Найдено	Разн	%	Инт	Стд Откл	
1	AC-2-614	.00011	.00009	.000	-11.7	.00001	.000	1
2	УстанСтд-1	-----	.00000	-----	-----	.00000	.000	-----
3	AC-2-616	.00049	.00052	.000	5.45	.00004	.000	1
4	AC-2-618	.00570	.00549	.000	-3.75	.00039	.000	1
5	CH-4	.00095	.00104	.000	8.95	.00008	.000	1
6	CH-7	.01060	.01071	.000	1.08	.00075	.000	1

Graph 2: Bismuth 190.241nm calibration

The calibrations are regularly checked against standard Quality Control samples (QCs) using iTEVA's user-friendly check table system. The results in Table 2 shows the excellent correlation between the measured values and the reference values of two Russian State reference materials.

Results

The Kolyma Refinery uses the iCAP 6500 Duo SSEA for routine analysis of low assay silver, high purity silver and other silver products. Table 3 presents results of some samples, in % weight units. The unknown concentrations were determined against the calibration curve using Concentration Ratio calibration mode. The detection limit was determined by the repeated analysis (10 replicates) of a high-purity silver sample, then multiplying the standard deviation of those results by 3 to produce a 3σ detection limit. Note that Sample # 1472-2 and Sample #1472-2' are duplicate samples to show the repeatability of the method.

	AC-2-614			AC-2-616		
	Ref. value	Found	SD	Ref. value	Found	SD
Ag	N/A	99.9940	0.0001	N/A	99.9180	0.0001
As	0.000113	0.00009	0.00002	0.00048	0.00052	0.00001
Au	0.00054	0.00050	0.00006	0.0025	0.00242	0.00009
Bi	0.000106	0.00009	0.00001	0.00049	0.00053	0.00002
Cd	0.000095	0.00008	0.00001	0.00044	0.00050	0.00002
Co	N/A	0.00023	0.00001	0.00028	0.00028	0.00001
Cu	0.00056	0.00056	0.00001	0.00267	0.00260	0.00006
Fe	N/A	0.00016	0.00003	0.0003	0.00030	0.00007
Mn	0.000126	0.00016	0.00001	0.00049	0.00049	0.00001
Ni	0.00011	0.00010	0.00001	0.00044	0.00042	0.00003
Pb	0.00044	0.00049	0.00001	0.0024	0.00240	0.00019
Pd	0.00052	0.00052	0.00001	0.00271	0.00270	0.00007
Pt	0.0005	0.00046	0.00001	0.0025	0.00261	0.00010
Rh	0.00046	0.00043	0.00001	0.00191	0.00191	0.00010
Sb	0.000235	0.00022	0.00001	0.00108	0.00103	0.00001
Te	0.00082	0.00085	0.00005	0.00302	0.00302	0.00013
Zn	0.00053	0.00052	0.00001	0.0021	0.00200	0.00001

Table 2: Correlation between found and certified values (all units in % w/w). SD is the Standard Deviation of the replicates of each element.

	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

Table 3: Results of a typical analysis with duplicates (1472-2, 1472-2') and detection limits (all units in % w/w)

Conclusions

Close monitoring of all stages of the silver refinery process is made possible with an iCAP 6500 coupled with an SSEA accessory, providing rapid, timely analyses with minimal sample preparation.

Thermo Scientific iCAP 6500 Duo-SSEA provides trace analysis of the impurities in pure silver. The data shows high sensitivity, multi-element determination of impurities at ppm and sub-ppm levels in a silver matrix as well as the ability to determine silver content itself.

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