



Determination of Indium (In) in electronic scrap

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In the past, Indium was used in different technical applications like in bearings, which have to withstand highly demanding working conditions like e.g. in aircraft engines. Another application is the use in sodium-vapour lamps to increase the efficiency and the luminosity. In the nuclear field, the alloy Ag80In15Cd5 is used to manufacture absorber rods for nuclear reactors.

Nowadays, In becomes more and more of interest because it is used as Copper-Indium-Gallium-di-selenide and Copper-Indium-sulphide for the production of solar cells and Indium orthoborate InBO_3 is used in computer screens to increase the stability of the image. High purity In (6N quality and above) has found a lot of applications in electronics like e.g. InP single crystals. Therefore, it becomes more and more of economic interest to recycle this material. Noteworthy amounts of In are together with precious metals in electronic scrap. As there are few certified reference materials (CRM) on the basis of electronic scrap on the market available, it was decided, to develop a new CRM. Following this decision a "round robin" with a fabricated sample under the direction of the German Federal Institute for Materials Research and Testing, BAM (Bundesanstalt für Materialforschung und -prüfung), Berlin.

Several members of the German GDMB Working Group for Precious Metals participated in this round robin. As well as In, ancillary elements Ag, Au, Be, Cu, Ni, Pd and Pt had to be analyzed. But it was quickly apparent that the determination of In was very difficult. The first result was 88 mg/kg with an uncertainty of ± 25 mg/kg. Because these results are not acceptable for a certified reference material, the German HORIBA Scientific ICP-OES application lab was asked to participate with its high resolution ICP-OES.

Sample preparation for a semi quantitative analysis CLIP

To find appropriate emission lines for the analysis by ICP-OES it is necessary to know the matrix element and also the concomitant elements. In the case of electronic scrap the problem is, that the scrap comes from different sources and can include a lot of different elements in different concentration ranges.

Another drawback is the general preparation of the starting raw material for the CRM. 50 kg of the starting material was crushed, incinerated and melted with 50 kg pyrite. The cast was crushed again and powdered to a grain size of 0.2 mm. Therefore, a high concentration of Fe was introduced into the material which leads to potential spectral interferences.

For an fast and easy semi quantitative analysis 1 g of the sample was melted with 10 g sodium peroxide in a Zr crucible. After digestion in acid and making up to a defined volume, the solution was analyzed with a semi quantitative program. In total, 58 elements were analyzed.

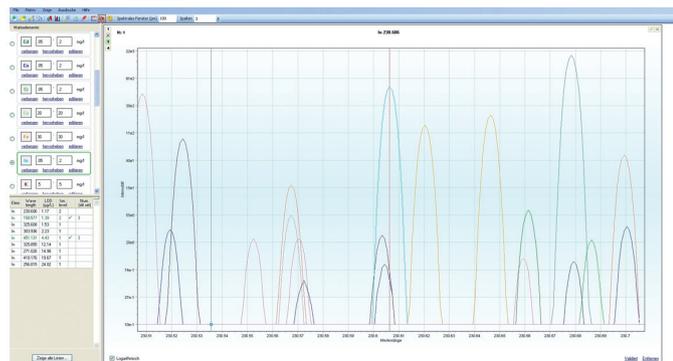
The result of this semi quantitative analysis was the basis for the CLIP software program (CLIP = Collection of Line Intensity Profiles) to extract appropriate emission lines for the analysis of In.

CLIP can extract emission lines in any matrices by taking into account the concomitant elements, the concentration of the concomitant elements, the resolution of every emission line and, in combination with the used Ultima 2 ICP-OES spectrometer, also the slit combination. The data base of CLIP contains more than 56,000 emission lines. Every emission line is characterized by its' detection limit, saturation limit, resolution and its' status (I or II). With all this information, CLIP can propose useful emission lines for a given analytical task. In the case of electronic scrap in total the influence of 27 elements were checked on In.

The influence of the other elements like the rare earth elements were found negligible, because the semi quantitative analysis shows no significant concentrations. Taking into account all elements and parameters, CLIP proposed two useful emission lines for the determination of In: 158.577 nm and 451.131 nm. Due to the better detection limit (1.4 $\mu\text{g/L}$ instead of 4.4. $\mu\text{g/L}$) and the better resolution (5 pm instead of 10 pm) for the further investigations only the emission line at 158.577 nm was used. One of the major advantages of CLIP is that it is always possible to see why an emission line was rejected by the program. An example of an rejected emission line is given in Picture 1. In Table 1 the prominent emission line of In are listed as well the interfering elements.

Table 1: prominent In emission lines and interfering element

In wavelength in nm	Detection limit in µg/L	Interfering element in nm
230.606	1.2	Co 230.604 Ni 230.603
158.577	1.4	---
325.608	1.5	Mn 325.614 Mo 325.621
303.936	2.2	Cr 303.932 Fe 303.940
451.131	4.4	---
325.855	12.1	Mn 325.841 Ti 325.864
271.026	15	Cr 271.028 Mn 271.033 Mo 271.019
410.176	19.7	Ar 410.173
256.015	24	Co 256.005 Fe 256.028 Mn 256.017



Picture 1: Profile of the rejected In emission line at 230.606 nm with an Ni and Co interference

Principle

The elemental analysis of the sample was done by Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES). The sample is nebulized and then transferred with an argon carrier gas stream into an argon plasma. The sample is desolvated, atomized and ionized, whereby the atoms and ions are excited.

The intensity of the light is measured when the atoms or ions return to lower levels of energy. Each element emits light at characteristic wavelengths, which can be used for the identification of the element. The intensity of the light is used for the quantification.

Instruments and operating specification

The work was done on a HORIBA Scientific ULTIMA 2 Dual grating ICP spectrometer. The specifications of the instrument are listed in Table 2, the specifications of the sample introduction system in Table 3, and the operating conditions of the instrument in Table 4.

Table 2: Specification of the ICP spectrometer ULTIMA 2 Dual grating

Parameter	Specification
Optical mounting	Czerny Turner
Focal length	1 m
Nitrogen purge	Yes
Gratings: number of grooves per mm	2400 g/mm and 4343 g/mm used in first order
Resolution	5.5 pm 120-440nm 10 pm 440-800nm
Type of generator	Solid state, water-cooled
Frequency	40.68 MHz
Torch	Vertical with Radial viewing and Total Plasma View*

* Total Plasma View: Measurement of the whole Normal Analytical Zone for enhanced sensitivity and reduced matrix effects

Table 3: Specification of the sample introduction system

Parameter	Specification
Nebulizer	Seaspray
Spray chamber	Cyclonic glass
Sample uptake	1 mL/min
Argon humidifier	Yes
Injector tube inner diameter	3 mm

Table 4: Operating conditions of the spectrometer

Parameter	Specification
RF generator power	1150 W
Plasma gas	12 L/min
Auxiliary gas	0 L/min
Sheath gas	0.2 L/min
Nebulizer pressure/argon flow	2.6 bar / 0.71 L/min

The acquisition parameter for the analysis are given in Table 5.

Table 5: Acquisition parameter

Acquisition mode	Max mode
Measurement points	1
Integration time	5 s
Entrance slit	20 µm
Exit slit	15 µm

Sample preparation and calibration samples

Three individual samples and also the standards were prepared by the Allgemeine Gold- und Silberscheideanstalt in Pforzheim.

The calibration samples were matrix matched with the following elements and concentrations: 150 mg/L Al, 750 mg/L Cu, 1500 mg/L Fe, 50 mg/L Sn and 100 mg/L. The samples were digested by the following procedure: 5 g sample were dissolved in 75 mL HCl (37 %) and heated for 30 min at 85 °C. Adjacent 50 mL HNO₃ were added and heated again for 2 h at 85 °C and again 50 mL HCl were added.

After the solution cooled down, 5 mL of HF were added. The solution was left over night and filtered. The concentration of the indium standard solutions is given in Table 6.

Table 6: Concentration of the Indium standard solutions

Standard solution	Concentration in mg/L
S1	0.2
S2	0.5
S3	1.2

Results

The result obtained for the analysis of In is given in Table 7. The value obtained with the ULTIMA 2 is very close to the average value with an excellent uncertainty. The average of the round robin is also given in Table 7.

Table 7: In concentration in the electronic scrap sample

Element	In concentration	Uncertainty
HJY result	90 mg/kg	± 1 mg/kg
Average round robin	91 mg/kg	± 7 mg/kg

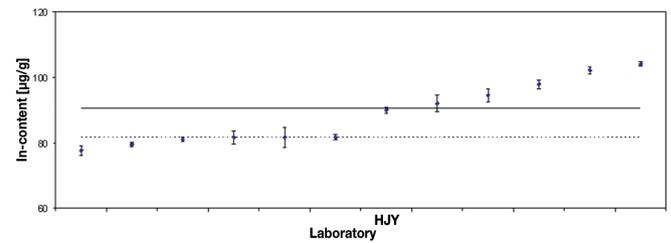
Conclusion

This application report demonstrates the strong advantage of the combination of different tools for the development of a method for the analysis of elements in difficult and line rich matrices.

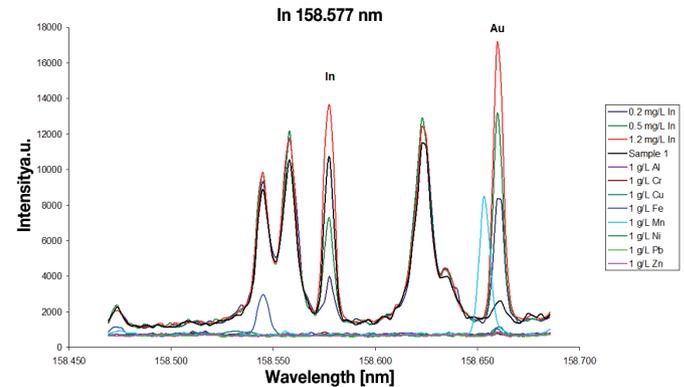
The fast semi quantitative analysis is with his results the basis for the CLIP software tool to extract useful emission lines. These tools, in combination with the excellent optical resolution, stability, sensitivity and VUV capability to be able to determine elements in the region below 160 nm with ICP spectrometers from HORIBA Scientific, allows the analysis of In in a difficult matrix without manipulation and extra work through mathematical procedures like inter element correction or deconvolution. The avoidance of software corrections improves accuracy and precision.

The reference material analyzed in this study will be available soon from BAM in Berlin (ERM®-EZ505). For more information see www.bam.de

Appendix A: Results of the round robin



Appendix B: Profile of the In 158.577 nm emission line (matrix matched standards and base metals with a concentration of 1 g/L)



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