

Rapid Evaluation of Smelting Copper Compounds Using Automated Multivariate Statistical Phase Analysis of EDS Spectral Imaging Data

Dr. Mitsuhiro Wada, Corporate R&D Center, Mitsui Mining & Smelting Co., Ltd., Japan

Introduction

In non-ferrous metal smelting operations, each element is refined from very complex compound material in which the major elements are Cu, Zn and Pb. When smelting Cu, it is very important to understand the complex morphology of the various compounds in the raw material. This detailed understanding of the complex morphology is necessary to improve the refining efficiency of each element. Currently, inductively-coupled plasma (ICP), X-ray diffraction (XRD) and electron probe microanalysis (EPMA) are used for the evaluation of the raw materials. However, ICP and XRD can only provide information about average, bulk composition.

EPMA may take several hours to do a quantitative analysis of a complex sample containing 10 to 20 elements and many phases. EPMA also requires highly experienced analysts to operate the instrument and evaluate a mixed compound material by using electron image contrast.

Recent developments in Silicon Drift Detectors (SDD) have improved the detection efficiency of energy-dispersive spectroscopy (EDS) and significantly reduced acquisition times. Robust peak deconvolution methods have improved the quality of EDS spectral imaging data to near that of EPMA. Furthermore, the introduction of EDS multivariate analytical methods simplify the analysis of phase distributions as opposed to just elemental distributions.

In this study we analyzed Cu-compound raw material by phase analysis using the multivariate statistical analysis of EDS spectral imaging data (Thermo Scientific COMPASS software). Even though the acquisition time was very short (30 minutes) relative to EPMA or ICP, we could determine the complicated distribution of the various phases.

Experimental Details

We evaluated Cu compounds which were generated in the initial process of copper lead smelting after the extraction of coarse lead. The distribution of the elements and the phase morphology were analyzed using a field emission scanning electron microscope (FESEM) and EDS. The analyzed area (a 230 × 180 μm rectangle) was observed by reflected light optical microscopy for metallic components. EDS data acquisition was done by SDD (Thermo Scientific UltraDry detector) and real time multivariate statistical phase analysis was performed during the data acquisition.

The sample was polished and coated with carbon for the EDS analysis in the FESEM.

Acquisition Conditions

EDS Analyzer:	NORAN System 7
EDS Detector:	UltraDry 30 mm ²
Accelerating Voltage:	12 kV
Magnification:	400×
Mapping Resolution:	256 × 192
Acquisition Time:	30 minutes
Stores Rate:	19,600 cps
Dead Time:	22%

Results and Study

Figures 1 and 2 show the electron image and the cumulative EDS spectrum for the EDS spectral imaging acquisition. The cumulative spectrum indicates that there may be a

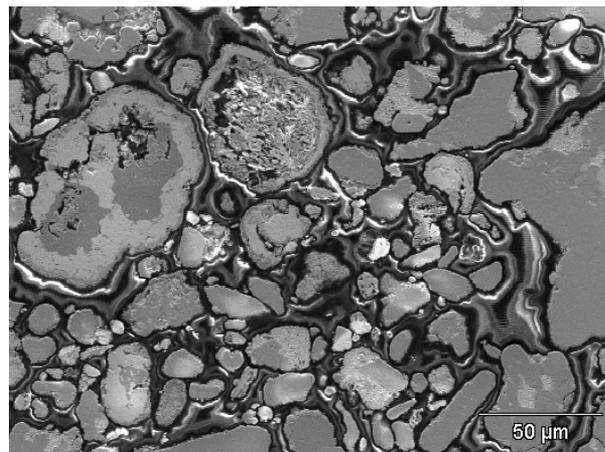


Figure 1: Secondary electron image

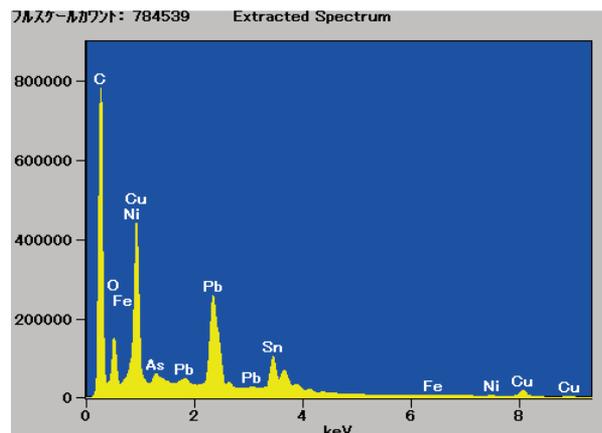


Figure 2: The cumulative spectrum for all of the pixels in the data set

Key Words

- COMPASS Software
- Mining
- Ore Analysis
- Peak Deconvolution
- Quantitative Mapping
- Smelting

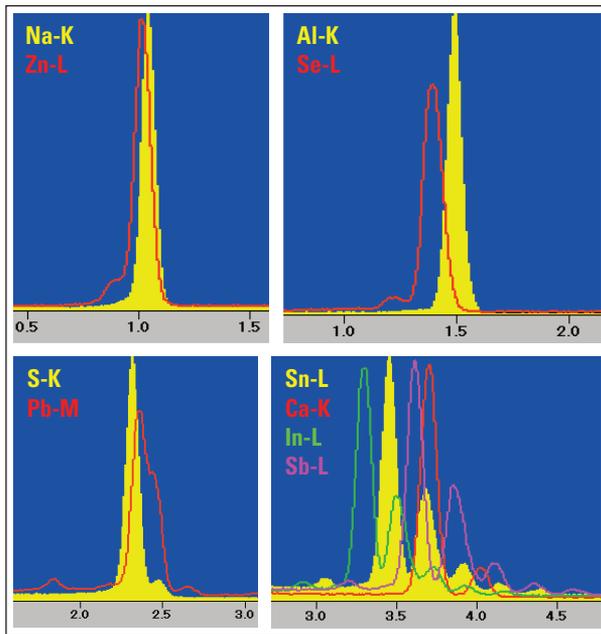


Figure 3: Peaks of characteristic X-rays of analyzed elements

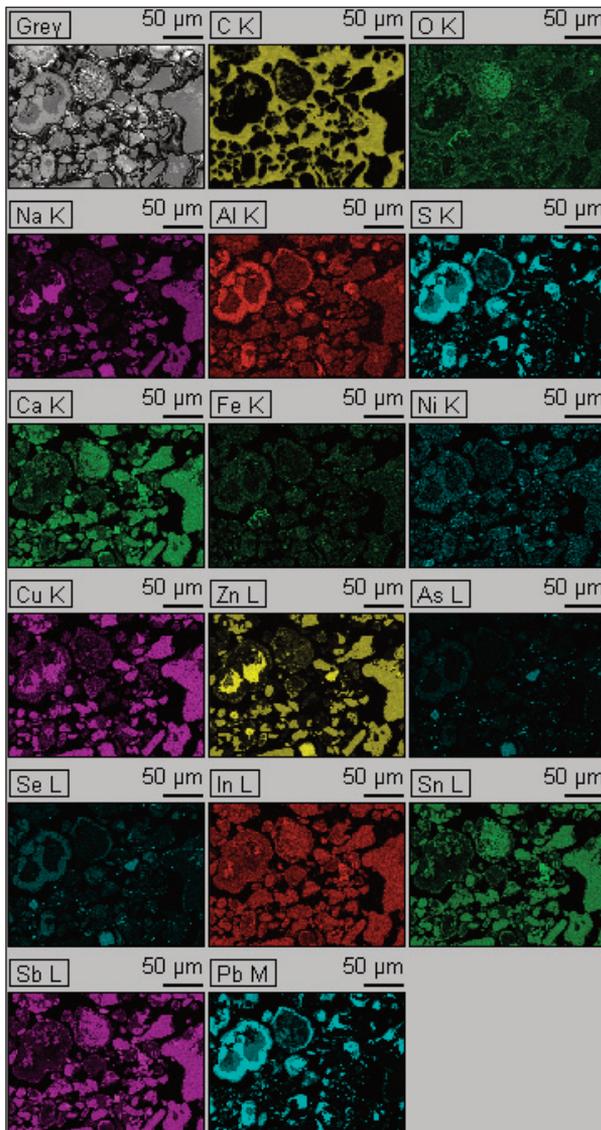


Figure 4: Conventional peak count maps

variety of potential peak overlaps of different elemental peaks. Figure 3 provides illustrations of a few of these overlap conditions.

Figure 4 shows the elemental distributions using conventional peak count maps. Any peak overlaps identified by Figure 3 are not corrected in these maps. These overlaps may provide false element intensities that will affect the interpretation of the spatial distribution of the elements.

Figure 5 shows the results of the peak deconvoluted quantitative elemental maps. It displays the real distributions of S, Sb, Ca, Al which were not shown properly in the conventional peak count maps because of overlapping peaks of other elements.

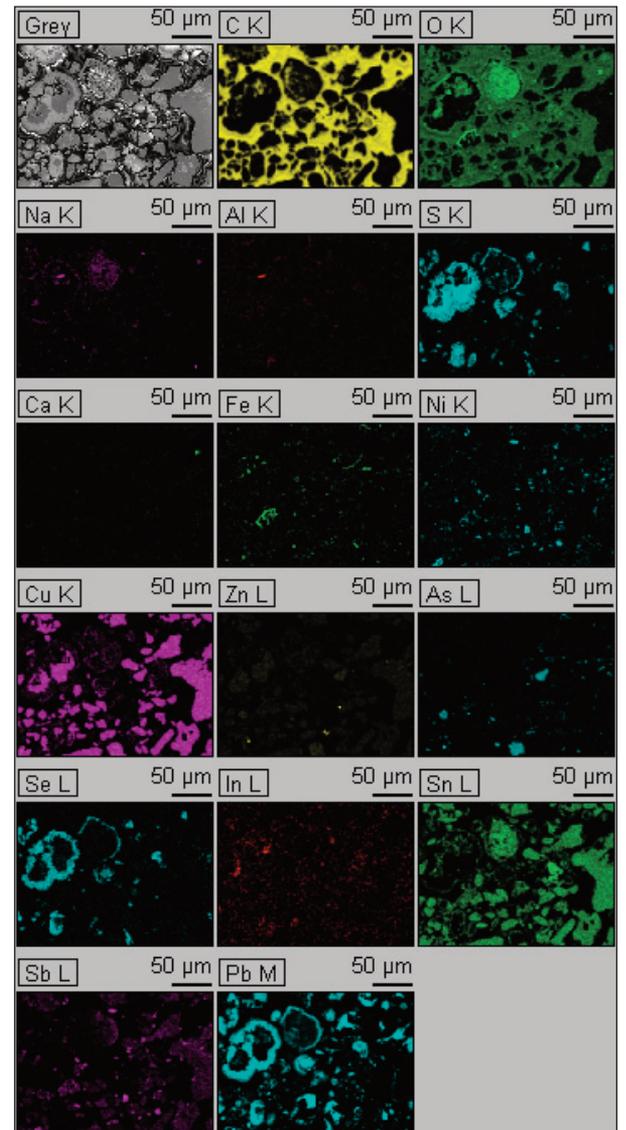


Figure 5: Quantitative spectral images

Figure 6 show the principal component maps extracted by COMPASS multivariate imaging analysis software, which processes and displays during the data acquisition.

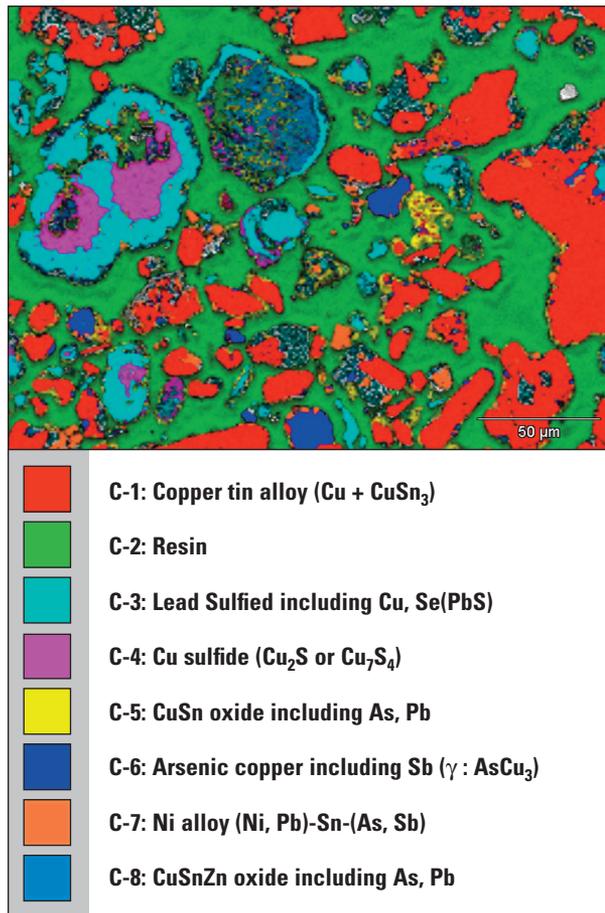


Figure 6: The first through eighth component maps of the 16 components extracted by COMPASS multivariate analysis software clearly show the morphologies of the Cu compounds which are difficult to understand thorough element maps alone.

The spectra of the first through the eighth principal components and the standardless quantitative results of the spectral data where the intensities of each component are especially strong are shown in Figure 7.

From these results, it became clear that the Cu compounds evaluated in this study have the following morphology of the elements and the distributions.

1. The main phase is a Cu-Sn alloy phase.
2. A Cu-Sn alloy phase exists as an associated phase with the Pb metal phase.
3. A combination phase consisting of oxides of Cu-Sn-Pb and Cu-sulfide exist as a nucleus which is encased by Pb-sulfide.
4. The glass component phase (C-9) and calcium fluoride phase (C-16) were easily distinguished. These components are very difficult to detect by EPMA if their presence was not expected.
5. S in Pb was identified which is very difficult to evaluate by conventional EDS element mapping. The typical distributions of small amounts of As, Se, In, Sb included in Cu-Sn alloy were clearly identified.

The evaluation of these results plays a key part in identifying and improving the processing steps to improve the efficiency of refining Cu compounds. Although the data acquisition time was only 30 minutes, the analytical data is complete. These rapid results ensure an improved throughput to the refining process.

Furthermore by evaluating materials produced in each refining process with this analysis method, the verification work of the material becomes very easy and simple.

Spectral Details of Overlapping Peaks

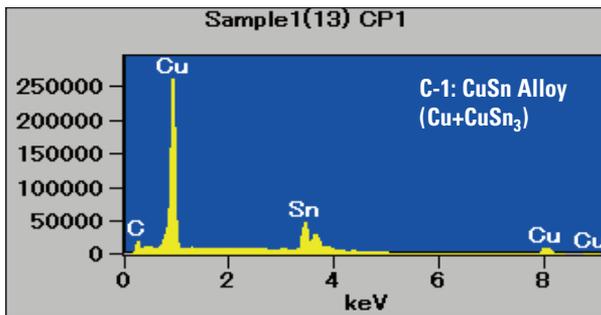
EDS has the following advantages over EPMA in that it can acquire the X-rays of the whole energy range simultaneously and collect X-ray maps at very low magnifications (less than 1000×) without requiring microscope stage scanning. However, this sample exhibits numerous combinations of elements where the characteristic EDS X-ray peaks overlap. Therefore, up to this point EPMA had been used to analyze these samples.

The conventional peak counts map (Figure 4) method simply extracts the X-ray counts in a given energy range of the peaks. Therefore, it may include X-ray counts of other element peaks which overlap. For example, the Al-K map has information from the Se-L peak, while the Ca-K, In-L, and Sb-L maps have information from the Sn-L peak. The S-K map is very similar to the Pb-M map.

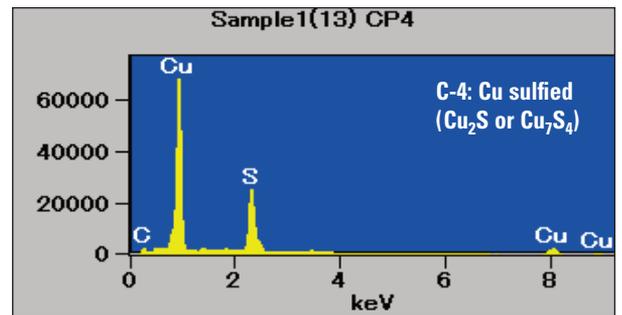
The deconvolution method for maps (Figure 5) is exactly the same as that routine for individual spectra except that it is applied to a kernel of pixel spectra for enhanced statistics. The corrective steps are as follows:

1. Remove the background (brehmstrahlung) of the EDS spectrum.
2. Separate the contributions of each element from overlapped peaks and provide net count maps.
3. Apply the appropriate matrix corrections to display atomic or weight percent data.

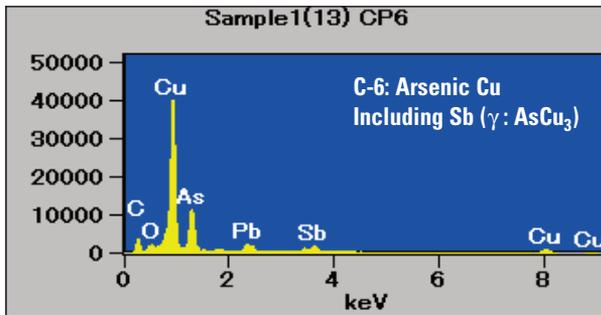
The spectral image results are very similar to those collected from the EPMA which uses wavelength-dispersive spectroscopy with higher spectral resolution. However, it is very difficult to understand the morphology of the chemical compounds from elemental maps.



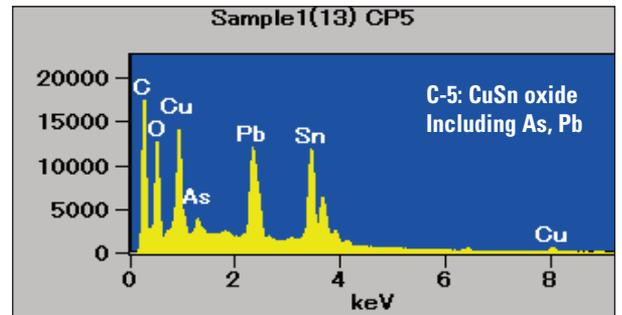
Element Line	Weight %	Atom %
<i>Cu L</i>	76.11	85.61
<i>Sn L</i>	23.89	14.39



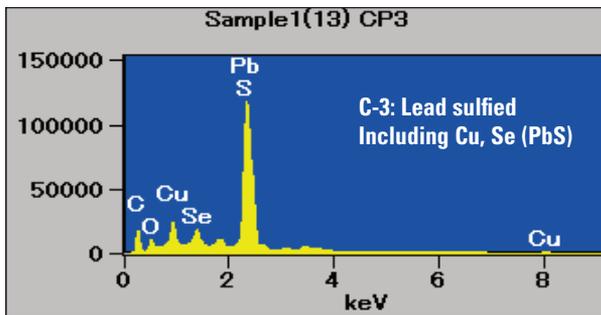
Element Line	Weight %	Atom %
<i>S K</i>	24.09	38.62
<i>Cu K</i>	75.91	61.38



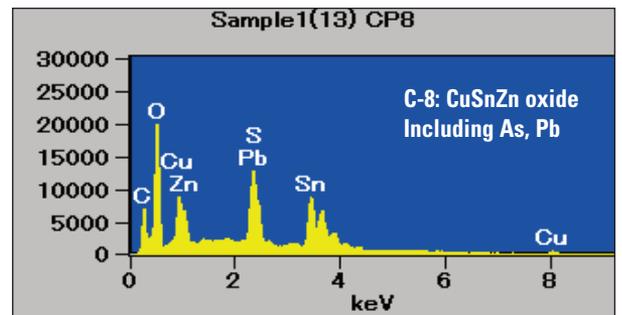
Element Line	Weight %	Atom %
<i>Cu L</i>	70.07	74.32
<i>As L</i>	26.32	23.68
<i>Sb L</i>	3.61	2.00



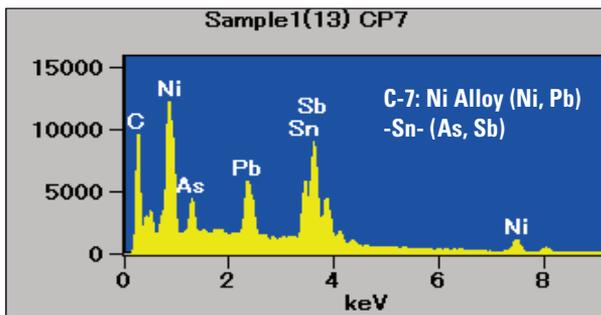
Element Line	Weight %	Atom %
<i>CK</i>	5.09	17.27
<i>OK</i>	21.61	55.04
<i>Cu K</i>	8.96	5.75
<i>As L</i>	2.84	1.55
<i>Sn L</i>	56.59	19.43
<i>Pb M</i>	4.90	0.96



Element Line	Weight %	Atom %
<i>SK</i>	11.74	42.64
<i>Cu L</i>	2.38	4.36
<i>Se L</i>	5.21	7.68
<i>Pb M</i>	80.67	45.32



Element Line	Weight %	Atom %
<i>CK</i>	4.50	13.89
<i>OK</i>	26.01	60.25
<i>SK</i>	1.11	1.28
<i>Cu L</i>	11.45	6.68
<i>Zn L</i>	6.78	3.85
<i>Sn L</i>	28.61	8.94
<i>Sb L</i>	10.06	3.06
<i>Pb M</i>	11.48	2.05
Total	100.00	100.00



Element Line	Weight %	Atom %
<i>CK</i>	2.28	15.13
<i>Ni L</i>	29.87	40.50
<i>As L</i>	3.58	3.81
<i>Sn L</i>	18.07	12.12
<i>Sb L</i>	39.72	25.96
<i>Pb M</i>	6.47	2.49

The second principal component was omitted because it is mounting epoxy.

Figure 7: Principal Component spectra by COMPASS and the standardless quantitative results of the raw data of the area where each component intensity is typically strong.

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

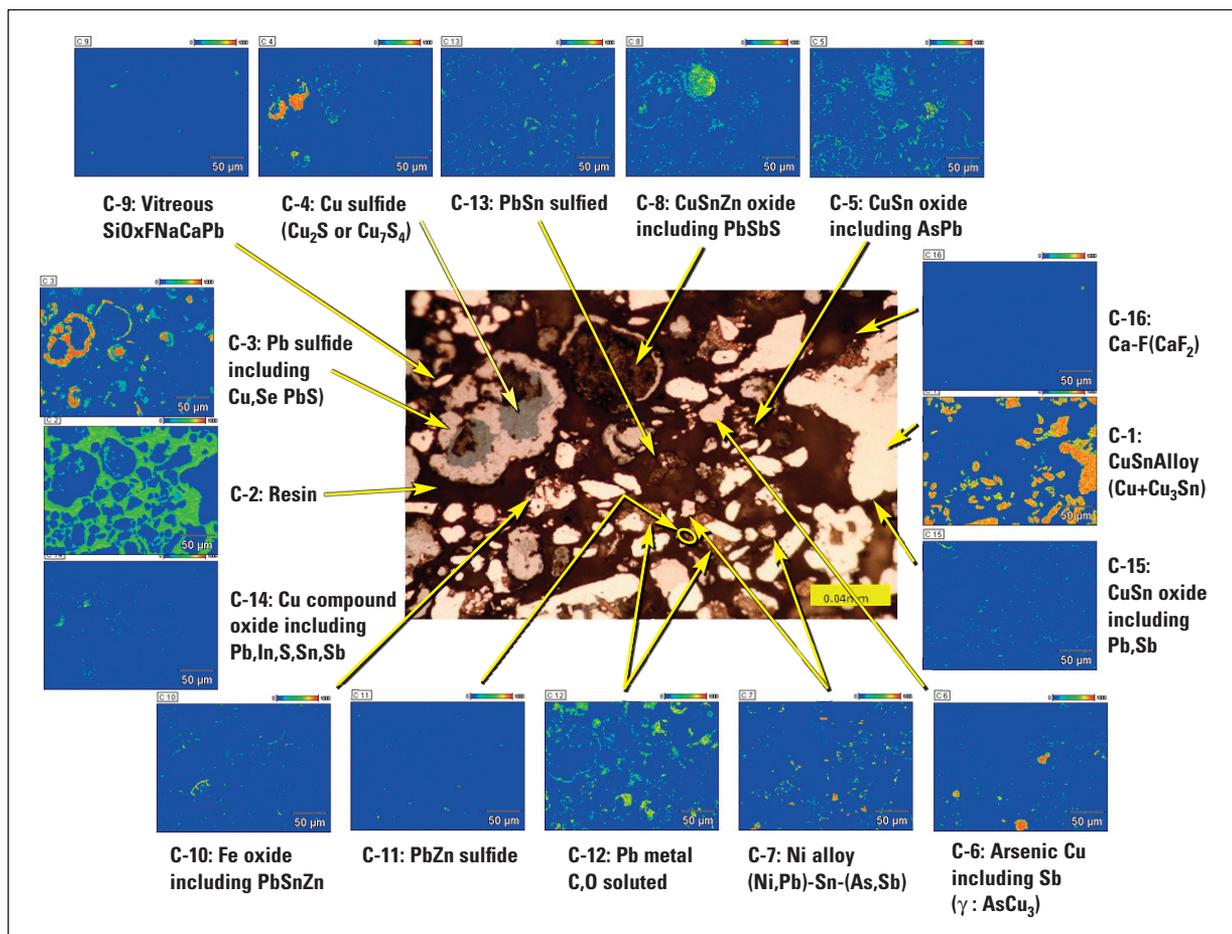


Figure 8: Sixteen phases automatically extracted by COMPASS software

Conclusion

By using multivariate statistical analysis software (COMPASS), we could easily and rapidly determine the morphology, distribution and chemistry of each distinct compound generated in the initial process of copper lead smelting. This lead to adjustment of the refining process and a cost savings to the smelting process.

Reference

M. Wada, *Journal of Advanced Science*, 22(2010)1-6.

Africa-Other
+27 11 570 1840

Australia
+61 3 9757 4300

Austria
+43 1 333 50 34 0

Belgium
+32 53 73 42 41

Canada
+1 800 530 8447

China
+86 10 8419 3588

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