ISOFORMATION OF SAMPLES FOR OPTICAL AND X-RAY EMISSION SPECTROGRAPHY

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The X-ray fluorescence method is characterized by a very high precision owing to stationary conditions at the excitation. This is also valid for the newly developed tape method in optical emission spectrography, when used in connection with a direct reading instrument.

In the tape method the sample is fed as a powder on to an adhesive tape, which passes through a spark gap [1]. All sparks are equivalent, since every single one evaporates new material.

A good reproducibility is necessary but not sufficient for an accurate analysis. Parameters such as particle size, chemical composition and chemical structure also affect the line intensities. Systematical errors are introduced if the sample and the standard differ with respect to these parameters.

The analytical program of the Boliden Mining Company comprises the determination of a large number of elements in a great variety of samples, such as ores, ore dressing products and smelter products. In order to rationalize and simplify this analytical work, we have tried to develop new universal methods using optical and X-ray spectrography in combination with a suitable pretreatment of the samples.

The new word *isoformation* has been introduced for this type of pretreatment [2]. To isoform samples means to makes samples of different origins fit the same analytical curves. The procedure of isoformation also makes it possible to prepare standard samples of any desired composition from pure elements and compounds. In other words, the standardization will be independent of wet chemical analysis of standard samples.

TYPES OF ISOFORMATION

Four main isoformation methods have been developed for spectrochemical analysis with the tape technique: (*1*) grinding with buffer; (*2*) fusion isoformation; (*3*) ion exchange isoformation; (*4*) sulphide isoformation.

The time required for making a complete analysis is 10–15 min when using isoformation methods 1 and 2 and about 30 min when using methods 3 and 4.

With suitable modifications these methods may also be applied in connection with X-ray fluorescence analysis.

DESCRIPTION OF THE DIFFERENT ISOFORMATION METHODS

Grinding with buffer

The sample is ground with a mixture of spectroscopic buffer, internal standard and wetting agent. The mill used by us is the "Schwingmühle" from Siebtechnik, Mühlheim. This mill gives a very efficient and reproducible grinding. It is also used for the grinding step of the other isoformation methods.

Grinding with buffer is an incomplete isoformation method. It does not eliminate the influence from differences in chemical structure. When determining elements being constituents of hard minerals, such as chalcopyrite it may also be difficult to completely eliminate influences due to particle size variations.

Fusion isoformation

The fusion method can be applied for slags and other oxidic materials. The sample is melted at 1000°C with a prefused lithium-strontium-tetraborate buffer in a graphite crucible. The fusion time is 5 min.

Cobalt oxide is included in the buffer as internal standard. The melt is poured on a water-cooled silver plate, and the resultant bead is ground in the "Schwingmühle".

Ion exchange isoformation

In the ion exchange isoformation method the different elements of the sample are transferred to a cation exchange resin, which is analyzed as a powder. The procedure is as follows (Fig. 1).

The sample is dissolved in acids. For sulphidic material perchloric acid is most suitable. It forms no complexes with the metallic ions and the dissolution is very fast. The excess of acid is removed by evaporation to near dryness.

Cadmium perchlorate is added to the solution as an internal standard and potassium carbonate as a spectroscopic buffer. The solution is deionized in a batch process by adding cation and anion exchangers.

The cations of the solution are collected by the cation exchanger and the anions by the anion exchanger. To speed up the process the solution is heated. The completeness of reaction is checked with a pH paper.

The cation exchanger and the anion exchanger have different particle sizes and are therefore easily separated from each other by a screening process. This separation is made in a plastic funnel equipped with a screen and a filter paper and connected to vacuum. The fine-grained cation ex-
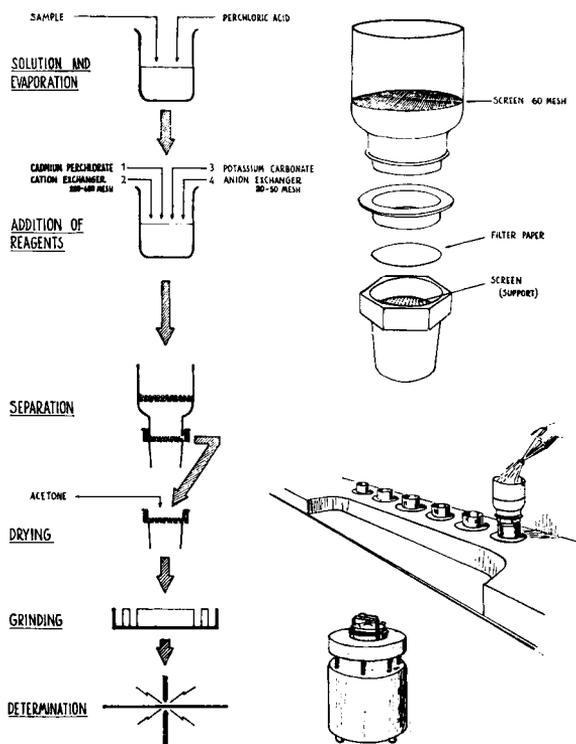
Fig. 1.—Process scheme for ion exchange isoformation and details showing some of the equipment: separation funnel, desk for separation and drying, and mill.

changer is washed down on to the filter paper in the lower part of the funnel with the aid of a shower of distilled water. The coarse anion exchanger remains on the screen in the upper part of the funnel.

After removing the screening part of the funnel, the cation exchanger is dried by washing with acetone and suction of air through it for a few minutes. The separation and drying of several samples is made simultaneously on a specially constructed desk.

As in the other isoformation methods the last step is the grinding. If the ion exchanger contains metallic ions which are electrolytically reduced by iron, e.g. copper, the grinding must be performed in mill houses of stainless steel to avoid metallic deposition.

The powder obtained by ion exchange isoformation contains the atoms from the sample, the internal standard and the spectroscopic buffer in a very homogenous and intimate mixture. The precision attainable with the tape and the X-ray fluorescence methods is therefore very high, when using this type of isoformation.

The periodic chart of Fig. 2 shows the most important elements which

Fig. 2.—Periodic chart showing the elements that can be analyzed using ion exchange isoformation.

can be collected quantitatively by a cation exchanger in a batch process. Some of these, such as the rare earths, uranium and thorium, do not have sufficiently sensitive lines to be determined by the tape technique. In a few cases it may be difficult to obtain ions of the appropriate valency. Tin, for example, must be divalent to be collected by the cation exchanger. However, it is usually obtained as quadrivalent ions or is precipitated as metastannic acid when dissolving the sample.

A detailed description of the method will be published [3].

The ion exchange isoformation method has been applied in connection with the tape technique and an ARL Quantometer at the Boliden Ore Dressing Plant for about two years. Lead, copper and zinc have been analyzed with good results in the range from 0.01 per cent to concentrate levels. The same working curves are used for all the different products.

A drawback of the method in this application is that arsenic cannot be determined in the same analytical operation. Therefore, a new isoformation method has been developed, named sulphide isoformation. By this method the products of the Ore Dressing Plant are isoformed with a view to a simultaneous determination of all the elements of interest that can be analyzed spectrochemically.

Sulphide isoformation

In the sulphide isoformation method the elements are precipitated as sulphides from a weakly acidic solution.

The procedure is shortly as follows (Fig. 3). The sample is dissolved in nitric acid. The excess of acid is removed by evaporation to near dryness.

Magnesium ions are added in the form of a chloride-nitrate solution. The positive, divalent magnesium ions have a flocculating effect on the negatively charged colloidal particles of arsenic sulphide.

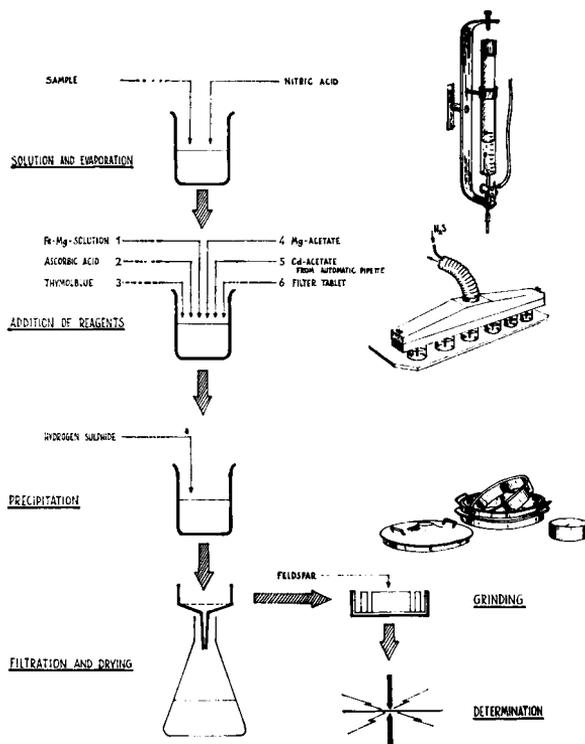To prevent the oxidation of hydrogen sulphide to elemental sulphur by

Fig. 3.—Process scheme for sulphide isoformation and details showing some of the equipment: automatic pipette, apparatus for precipitation, and mill house with mill bodies.

ferric ions, ascorbic acid is added. Ascorbic acid reduces the trivalent iron to the divalent form. The presence of a sufficient amount of chloride ion prevents a simultaneous reduction of copper ions to metallic copper.

pH is then adjusted with a magnesium acetate solution using thymol blue as an indicator. In order to obtain a simultaneous and complete precipitation of both zinc and arsenic, the pH at the precipitation with hydrogen sulphide has to be about 2.5. Cadmium is used as an internal standard. It is added as an acetate solution to diminish the change of pH during the precipitation.

Paper powder in tablet form is added as a collector for the sulphides. Hydrogen sulphide is then bubbled through the solution for 5 min. By heating the solution to near boiling during the precipitation period all the arsenic sulphide can be precipitated in a filterable form. The tendency of arsenic sulphide and of zinc sulphide to form colloidal precipitates has in fact significantly influenced the details of the method. The precipitation is performed in a specially constructed apparatus. Six samples are precipitated simultaneously. Capillaries in the upper part of the hydrogen sulphide inlet

Groups Periods	I	II	III	IV	V	VI	VII	VIII			P
1	H									He	1
2	Li	Be	B	C	N	O	F			Ne	2
3	Na	Mg	Al	Si	P	S	Cl			A	3
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	
	Cu	Zn	Ga	Ge	As	Se	Br			Kr	4
5	Rb	Sr	Y	Zr	Cb	Mo	Tc	Ru	Rh	Pd	
	Ag	Cd	In	Sn	Sb	Te	I			Xe	5
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	
	Au	Hg	Tl	Pb	Bi	Po	At			Rn	6
7	Fr	Ra	Ac								7

6	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	6
7	Th	Pa	U	Np	Pu	Am	Cm								7

Fig. 4.—Periodic chart showing the elements that can be analyzed using sulphide isoformation.

tubes guarantee an equal and constant rate of gas flow into all the beakers. The apparatus is provided with a hood connected to the exhaust system. The construction permits practically no hydrogen sulphide to enter the room.

Filtration is made by suction on nutches using a high retention filter paper. The retention of the filter paper is increased still further with the aid of very finely ground cation exchanger. The precipitate is dried as in the ion exchange isoformation method.

The precipitate and the filter paper are ground with feldspar. The latter is used as a spectroscopic buffer.

The sulphide isoformation method has two favourable properties. A high sensitivity can be achieved by enrichment, and the iron content of the samples is removed to such an extent that the line-rich iron spectrum is greatly eliminated.

The periodic chart of Fig. 4 shows the elements which may be determined by this method.

Fig. 5 shows some of the working curves for the determination of Cu, Zn and As with a direct reading spectrograph when applying tape technique and sulphide isoformation. The curves are based on synthetic solutions and natural samples with widely different composition.

DISCUSSION

When applied to optical emission spectrography with the tape technique fusion isoformation, ion exchange isoformation and sulphide isoformation completely eliminate systematical errors caused by variations in particle size, chemical composition of the sample and chemical structure.

In X-ray spectrography a complete isoformation is achieved with respect to only particle size and chemical structure. The influence of the chemical composition, usually referred to as the inter-element effect, can be reduced by dilution with heavy elements. However, such a dilution is seldom allowed
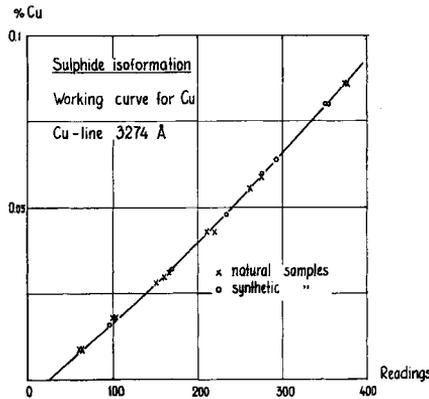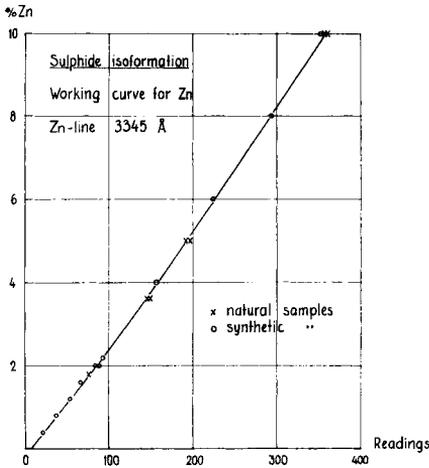
Fig. 5 *a*.
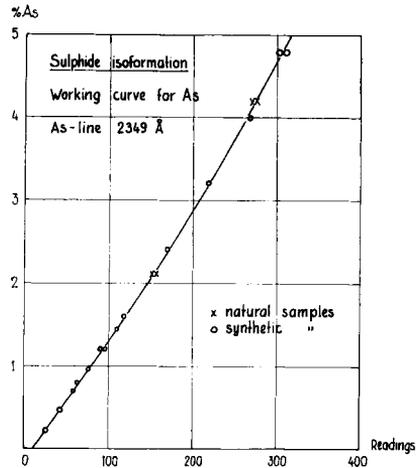

Fig. 5 *b*.   Fig. 5 *c*.

Fig. 5.—Determination of copper, zinc and arsenic with sulphide isoformation, tape technique and ARL Quantometer. Working curves for the analytical lines Cu 3274 (*a*), Zn 3345 (*b*), and As 2349 (*c*).

on account of loss in sensitivity. Another way to diminish the influence from the inter-element effect is to refer the measurements to suitable standards. In general, one internal standard has to be used for each element to be determined. There is only a small number of elements suitable as internal standards for a certain element, as the position of the absorption edges and the wavelengths of the X-ray radiation should differ as little as possible between the two elements. Difficulties are therefore likely to be encountered with samples of complex chemical composition.

The necessity of having several internal standards in X-ray fluorescence analysis is illustrated by Fig. 6. It shows working curves for lead and zinc in samples that consist of lead, zinc and low atomic number elements and
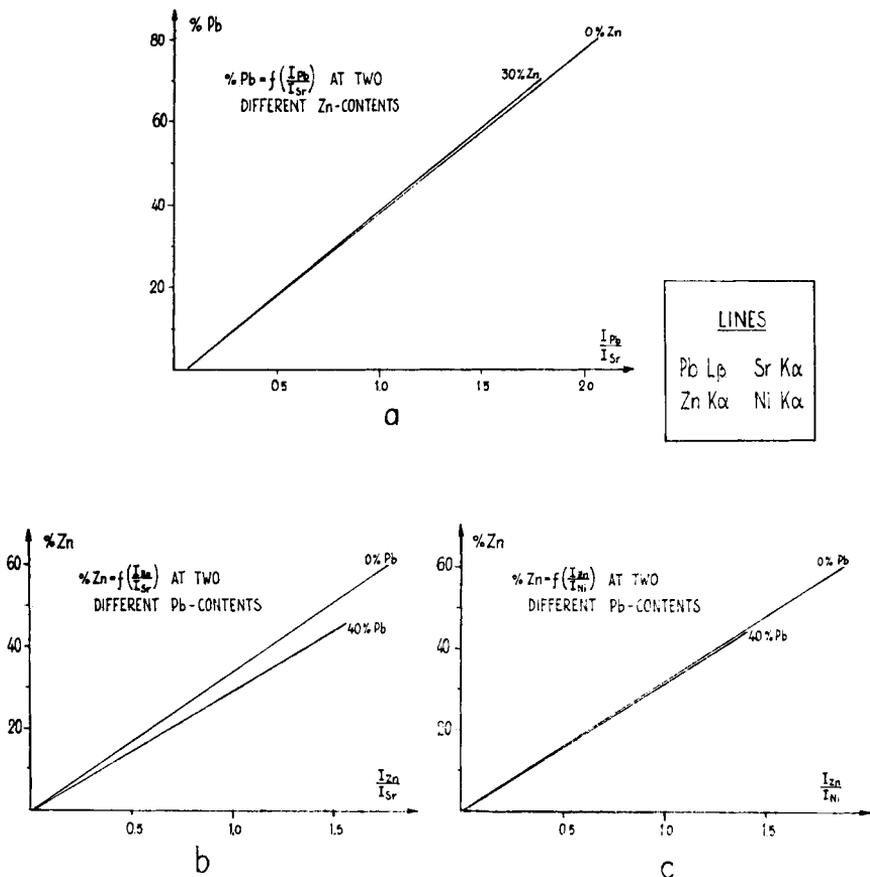
Fig. 6.—Working curves for X-ray fluorescence analysis on samples isoformed by ion exchange, showing the magnitude of inter-element effects when using different internal standards.

which have been isoformed by ion exchange. Sr $K\alpha$ is quite a good internal standard line for Pb $L\beta$ (6a). If Sr $K\alpha$ is used as an internal standard line for Zn $K\alpha$, strongly diverging curves are obtained for different contents of lead (6b). For Zn it is much better to use Ni as a reference element (6c).

In optical emission spectrography the main purpose in introducing of an internal standard is quite different. In the tape technique, for example, the internal standard mainly eliminates the random errors arising from variations in charging on the tape, vaporization and excitation. The precision obtained may be dependent on the internal standard. Cd, for example, is the most ideal internal standard found for Zn and In for Pb and Ag. In general, however, quite satisfactory results are obtained when utilizing only one internal standard for all elements.

SUMMARY

The isoformation methods have already for a number of years demonstrated their usefulness in connection with spectrochemical analysis with the tape method. To a limited extent they have also found application in X-ray emission spectrography.

By the introduction of isoformation methods optical and X-ray emission spectrography are made independent of wet chemical analysis of standard samples. Isoformation makes it possible to analyze samples with great variation in composition in a rational way using spectrochemical determination.

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