ANALYSIS OF NON-FERROUS METALS

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Abstract - In the U.K. the primary production of non-ferrous metals is very limited, the major part of the industry being concerned with recycling, i.e. secondary metal production. Apart from the analytical problem of ores and associate materials the analytical controls are similar to those used in the rest of the world.

The classical chemical methods of control have been largely superseded in these industries by physical instrumentation. The application of these methods has led to problems, i.e. standardisation and the extension of the technique to wider application is continuing.

Each part of the industry has had its individual problems and the application of modern techniques is best considered for each particular sector. The newer physico-chemical techniques have made a big impact on the ''wet'' chemical analysis, notably the application of atomic absorption techniques, both with flame and the non-flame source.

The inductively coupled plasma is a newer technique both for solid and solution samples and shows promise in the non-ferrous analytical field. However, the problem of environmental control is the field in which the analyst in these industries has become more involved, the methods of sampling and subsequent analysis becoming more and more important.

INTRODUCTION

In order to appreciate the direction that analysis of the non-ferrous metals and their alloys has taken over the recent years, it is necessary to look at the basis of their production.

Figure 1 sets out the production of copper and alloys in the U.K. and it may be seen that a large proportion is imported in refined forms, some 37% is used in wrought copper alloys, 55% in copper products and 8% in cast copper alloys. The analytical requirements are then concentrated at the point of modification, i.e. after refining and after the melting or remelting to alloys.

In the case of aluminium there is a considerable smelting capacity, producing some 50% of the total tonnage (Fig. 2) from imported purified bauxite. The major usage is into wrought products, the casting industry being fed largely from scrap recycling. The major analytical requirements are then the control of the smelting process, the control of the purity of the metal, and of the alloy production of both wrought products and ingots for the casting industry.

U.K. COPPER

U.K. ALUMINIUM

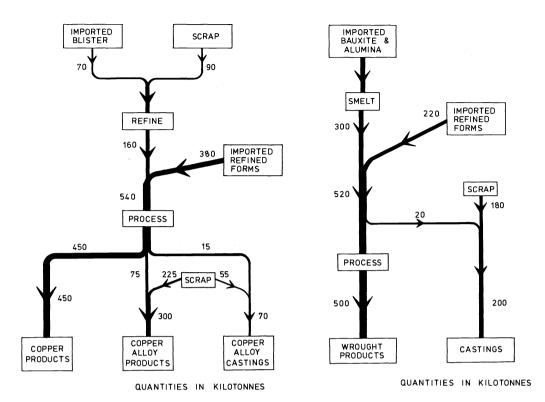


Fig. 1 Fig. 2

The lead industry is supplied almost entirely by imported bullion and recycled scrap (Fig. 3), some 30% of production being directed into chemicals, an amount almost equal to the importation, and lost to metal production. The analytical requirements are thus for the pure metal and the alloys.

Zinc production (Fig. 4), apart from a small smelting capacity, is supplied very largely by imported refined metal and the analytical requirement is similar to that of lead.

In three of the four major sections of the non-ferrous industry in the U.K. there is little or no primary extraction of the metal and the analytical effort has thus been concentrated into the control of metal purity and the process control of alloy production.

Because of the overriding need for speed of analysis in process control, physical methods of analysis, where the provision of solid samples are the preferred form, have taken over almost entirely from wet chemical analysis in this field. Particularly in recent years it has been realised in a number of areas that a real financial saving can result from analytical control to the cheaper end of a compositional range and quite small concerns, particularly in the copper alloy field, have installed physical instrumentation.

Attention will then first be given to the physical methods using solid samples.

OPTICAL EMISSION SPECTROSCOPY

Photographic recording

This technique is still used in the industries, particularly for the analysis of high purity metals and for the identification of alloy types.

U.K. LEAD

U.K. ZINC

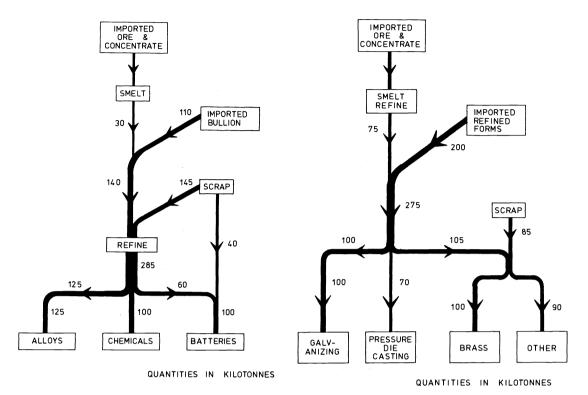


Fig. 3 Fig. 4

The globule arc technique for the analysis of high purity copper is common due to its simplicity of source, its high sensitivity for most elements and the qualitative aspect of the photographic plate technique. The sensitivities obtainable by the technique are shown in Table 1 where it may be seen that for the majority of elements an adequate sensitivity is obtained (1). The method needs careful sample preparation, operator skill in management of the arc and in interpretation of the spectra. The globule arc method is also applied in direct reading instrumentation and thus the photographic method is being phased out. The technique of point to plane excitation in argon and vacuum spectroscopy is also increasingly used.

Table 1. Sensitivities of the globule arc technique for the analysis of copper (photographic recording).

Element	Limits of detection (ppm)
Al	<1
Sb	1
Bi	0.5
Cd	<1
Fe	1
Pb	< 1
Mn	5
Ni	0.5
Ag	«1
Sn	1
Zn	5
As	10
P	-
Se	<10*
s	-
Te	10
Si	< 5

^{*}Long exposure and special plate

Little use is now made of the photographic recording method in the aluminium industries.

In the lead industry this method is used in some situations, almost invariably for the analysis of impurities, and the high voltage spark excitation technique in air is generally applied, the range of minor constituents determined being $0.0005\%^{(2)}$. The control of composition of zinc and its alloys has for many years been by photographic emission, using generally pin to pin samples and high voltage spark excitation.

In general the use of the photographic recording method is routine and, in particular, process control analysis is being rapidly superseded by direct reading methods.

Direct reading emission spectrometry

The aluminium industry is analytically served, both for nominally pure products and alloys, by the direct reading spectrometer. Table 2 shows the range of composition covered by the technique and levels of both residuals in the nominally pure material and alloying additions are well covered. The excitation used is usually point to plane in air and an air path spectrometer.

TABLE 2. Application of direct reading optical spectrometry to aluminium and its alloys.

Element	Range (%)
Fe	0.002-1.0
Si	0.002-15
Mg	0.0005-12
Mn	0.0005-2.0
Cu	0.005-12
Ni	0.001-3
Cr	0.005-1
Pb	0.005-1
Sn	0.001-0.2
Zn	0.001-6.0
Te	0.0005-0.5
Ве	0.0001-0.1
В	0.0005-0.1
Bi	0.0005-0.5
Ag	0.0005-1.0

There are, however, considerable matrix effects experienced in this procedure and it has been stated that, to cover a range of alloys, 108 separate calibration curves are necessary⁽³⁾. To alleviate this, the use of a nitrogen purged gap⁽⁴⁾ has been investigated by a large primary supplier and is accepted as routine in its plant laboratories. The technique produces calibration curves for

a number of alloy systems which lie very much closer to a common curve and closer to that obtained from binary standards. A typical set of calibration curves for zinc demonstrating this is shown in Fig. 5, where the 'master' calibration curve is shown as a solid line drawn using aluminium binary standards, these being indicated by filled symbols, and the improvement in 'fit' with nitrogen shielding may be seen. Part of the improvement, it is suggested, is due to a reduction of the inter-element effect in the internal standard spectral line which is reflected in the variation of exposure time and this effect is shown in Table 3 for a group of alloys excited in air and nitrogen.

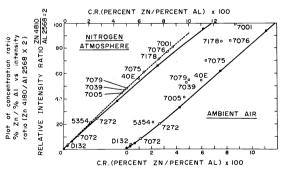


Fig. 5

The analysis of aluminium and alloys by optical emission has necessitated the production of both standard and sample under rigidly controlled conditions, typically rapidly chill cast into 'mushroom' type moulds.

The use of an argon atmosphere, an energetic pre-spark and a high repetition rate analytical discharge has been claimed to accomplish the same ends $^{(3)}$. The remelting of the sample in the 'burnt' spot is also thought to negate the influence of differing structures.

TABLE 3.	Variation in exposure period for aluminium alloys, air and nitrogen
	atmosphere.

Alloy matrix		Exposure	period (sec)		
		Air	Nitrogen		
Super pu	Super pure Al			20.0	20.0
Unalloye	d Al			21.7	19.6
4.5Cu	1.5 Mg	0.5Mn		28.8	19.5
2.5Mg				25.7	19.3
0.6Si	1.0 Mg			23.5	19.7
1.5Cu	$2.5 \mathrm{Mg}$	6.0Zn		31.8	19.4
12.0Si	1.0Cu	$1.0 \mathrm{Mg}$	2.5Ni	23.5	19.3
9.0Si	1.0Fe	3.5Cu		23.9	19.4
12.0Si				23.1	18.8
5.5Zn				26.9	19.3
10.5Mg				27.5	19.1

The efficiency of the single 'master' calibration aspect is demonstrated in Fig. 6, again for zinc, where the multiplicity of curves obtained in air could be said to condense into the single curve in argon. In a series of samples of different metallurgical structure and history it is claimed that intensity differences of up to 30% were obtained with an oscillating medium voltage discharge in air, up to 15% for a glow discharge according to 'Grimm' (5), 10% for a nitrogen purged discharge compared to 'differences that are not statistically certain''.

The application of direct reading spectrometry to the analysis of copper and its alloys is now turning to the use of argon excitation techniques, together with vacuum spectrometers, particularly for the elements with sensitive lines in the 170-235nm range (arsenic, sulphur, selenium).

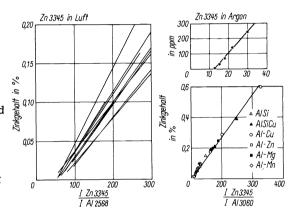


Fig. 6

Table 4 compares the sensitivities obtained by a point to plane, argon atmosphere, vacuum spectrometer method and the older established globule arc, photographic recording techniques. It can be seen that in a number of instances the argon excitation sensitivity approaches and exceeds that of the globule arc. As was mentioned in the previous section, this technique is taking over from the globule arc for the control analysis of copper metal.

For the analysis of copper alloys the range of application is extending towards and exceeding the 10% concentration level and in Table 5 a comparison is drawn between the XRF and the optical direct reading technique⁽⁶⁾ with regard to reproducibilities obtained at impurity and alloying constituent level, where it can be seen that in general the optical is equal to or better than the XRF figure at the impurity level of content, but that the XRF reproducibility exceeds that of optical direct reader at or about the 10% level of content.

Several control laboratories are reported to be routinely determining up to 40% zinc in brasses with sufficient accuracy for production control.

Inter-element effects are present in this context but are not as gross as experienced with aluminium alloys and are overcome by the use of standards of the same alloy types as the sample.

Lead and the more dilute alloys are analysed by the direct optical emission spectrometer and Table 6 shows the range of application of the technique. This is quite adequate for the control of the secondary refining processes and for the analysis of pure lead.

TABLE 4. Optical direct reading vs. photographic limits of detection for impurities in copper.

	Limit of detection (ppm)		
Element	Globule arc photographic	Point to plane direct reader	
Al	<1	2	
Sb	1	2	
Bi	0.5	2	
Cd	< 1	1	
Co	1	1	
Fe	1	3	
Pb	<1	4	
Mn	-	0.5	
Ni	0.5	2	
Ag	<1	2	
Sn	1	4	
Zn	5	10	
As	10	1.0	
P	-	0.4	
Se	< 10	6	
S	_	3	
Te	10	10	

TABLE 5. X-ray fluorescence analysis of copper base alloys, compared with optical direct reader.

Element	Range (%)	XRF reproducibility (%)	Optical emission (argon-vacuum) reproducibility (%)
Cu	(60 (90	0.05	-
Zn	(0.1	5	5
	(40	0 . 1	0.5
Pb	(0.02	10	5
	(10	1.0	1.0
Sn	(0.02	10	5
	(10	0.5	1.0
Al	(0.01	20	5
	(10	1	1
Fe	{ 0.02	5	5
	{ 5.0	1	1
Ni	(0.02	5	5
	(30	0.5	1
Mn	(0.02	5	5
	(3.00	1	1
P	{ 0.01	10	2
	{ 1.0	2	2

TABLE 6. Application of direct reading optical spectroscopy to lead and its alloys.

Element	Range (%)
As	0.0005-0.5
Sb	0.0005-5.0*
Bi	0.0001-0.5
Cd	0.0001-1.0
Cu	0.0001-0.1
Ag	< 0.0001-0.1
Ni	0.0005-0.1*
Sn	< 0.0005-2.0
Zn	< 0.0005-0.1
Te	0.0005-0.1
Tl	< 0.0005-0.1

^{*}Difficulties with segregation.

The application to the antimonial alloys is difficult due to segregation effects and this class of alloy, together with tin solders, is an area where XRF has found more application.

Zinc, and particularly the 'Mazak' or 'Zamak' type of alloys, has for many years⁽⁷⁾ been a subject for analysis by optical emission procedures and it was demonstrated as long ago as 1945 that, within the narrow specification limits applying, little or no inter-element effects occur (Table 7).

In the case of both lead and zinc an air excitation method is used with a pin to pin or point to plane geometry.

TABLE 7. Application of direct reading optical spectroscopy to zinc and its alloys.

Element	Range (%)
Al	0.0005-5
Pb	0.0002-1.0
Sn	0.0005-1.0
Fe	0.0005-1.0
Mg	0.0001-0.1
Cd	0.0001-1.0
Cu	0.0005-1.0
Ti	0.005 -0.5
Cr	0.005 -0.5

X-RAY FLUORESCENCE ANALYSIS

The aluminium industry has concentrated on, and in the main been well served by, the direct reading optical spectrometer and little use has been made of the XRF method in the analytical control of metal or alloy production. An important area where XRF is used is in the analytical control of the electrolyte in the Hall-Heroualt cells used in the primary smelting process. The process consists of electrolytically reducing alumina, dissolved in a flux of molten cryolite (3NaF.AlF3) with carbon electrodes. For efficient operation the 'bath ratio' or the sodium fluoride to aluminium fluoride ratio must be maintained within a constant range of 1.38-1.40. Calcium fluoride is added to lower the melting point of the bath.

The procedure $^{(8)}$ used is to measure by X-ray diffraction (XRD) the intensity of the chiolite (Na₅Al₃F₁₄) and fluorite (CaF₂) lines, which depend on the AlF₃ concentration. The concentration of CaF₂ directly affects the intensity of the XRD determination and a separate XRF determination of the calcium present is used to correct for this.

A different approach to the problem is the application of the electron beam excitation method where constituent elements (9,10) i.e. fluoride, sodium, aluminium and calcium are determined to calculate the bath composition. Additionally, with this technique, the oxygen content can be measured to give a figure for the dissolved aluminium to assist in the diagnosis of 'sick' pots.

It is in the field of copper and particularly copper alloys that the XRF technique has had its biggest impact. It is also used, where available, for the control of the secondary refining to copper, where the high level of impurities in some intermediates favours this technique rather than optical emission.

To apply the XRF method to the analysis of copper alloys, which are often highly alloyed systems, many studies $^{(11-15)}$ have been made into the inter-element effects encountered which can be gross. For example, in a 60/40 brass the presence of 0.4% lead will give a copper figure 0.3% low, 1.6% aluminium a figure 0.5% high and similar effects are experienced with most addition elements. These effects can be considered additive and a number of correction methods have been produced $^{(11-15)}$.

The very high precision of XRF analysis allows these, at times highly significant corrections, to be made and standard deviations of 0.05-0.11% copper for a routine copper determination in the range of 55-95% in alloys, requiring two or three inter-elements correction, have been quoted (16,17).

That the cost of installation of this equipment can be quickly recovered in the copper and copper alloy field has been demonstrated by a U.K. producer⁽¹⁸⁾. The yearly saving of manpower costs, controlling to cheaper specifications, lower remelting costs and lower running costs of the control laboratory was, at 1967 prices, some £14,000 per year.

The XRF analysis of lead alloys is also well established and the major concern has been with the segregation difficulties experienced with the high antimonial alloys which have been overcome by close attention to the chill casting of the sample and surface preparation $^{(1\,9)}$.

In the analysis of solder an effect of ageing of the sample has been reported⁽²⁰⁾. This problem has been overcome by allowing the standard reference materials to fully age, assigning apparent composition to each with reference to newly cast materials.

Both the optical direct reader and the XRF method are essentially comparative techniques, albeit of considerable precision and depend entirely on the provision of solid standards, in a similar metallurgical condition to the sample. Many laboratories are concerned with the production and with the authentication of these standards, which is current European convention to term 'reference materials'.

There are available to analysts two publications $(2^{1}, 2^{2})$ listing the sources of these materials and in general reference materials are available for the applications discussed herein. There are four main sources of supply:

- (i) The large metal suppliers, particularly in the aluminium and zinc fields.
- (ii) National agencies, i.e. National Bureau of Standards.
- (iii) International agencies, i.e. Community Reference Bureau of the EEC.
- (iv) Commercial independent suppliers such as the Bureau of Analysed Samples in the U.K. and Morris P. Kirk in the U.S.A.

It is probably true to say that most of the wet chemical analysis still being performed in the non-ferrous industry is concerned with the authentication of these materials, without which the fast, convenient and sophisticated instrumentation which has overtaken chemists in the routine field would be quite useless.

ATOMIC ABSORPTION ANALYSIS

The advent of this technique into the non-ferrous analytical field and publication of excellent reference books, particularly those slanted towards metals analysis, has led to rapid acceptance and wide use $(^{23})$.

The relative freedom from interferences, and hence little chemical work-up, assured its rapid penetration and the use of the technique, particularly in the analysis of reference materials discussed above, is widespread.

Smaller concerns, particularly in the copper alloy industry, used the technique as an interim measure between phasing out the analytical control by wet chemical procedures and the full implementation of physical methods. Table 8 demonstrates an example of how this might be done, using three instruments to perform the minor constituent analysis of a high tensile brass for process control. The analysis could be completed in ten minutes from receipt of sample, probably the maximum time that could be allowed for this analysis, if a melt were being held. The accuracy would not be adequate for the control of the zinc content.

TABLE 8. Atomic absorption analysis of high tensile brass.

Tin Min.	me Sec.	Action					
		Sample received					
0	0	Milled					
0	45	*** 1 1 40 5					
1	45	Weighed out 0.5g.					
3	00	Dissolved in HC1-HN	O_3				
3	00	Cooled and diluted to	50ml (solution A)				
5	00	Diluted 1:10 by autor	natic diluter (solution	B)			
Ti	me	Instrument A	Instrument B	Instrument C			
Min.	Sec.	Action Action Action					
		Read Al absorption N2O flame solution A Read Pb absorption Read Fe absorption solution B					
6	00	Chause laws	Charre laws	Change lawn			
		Change lamp Reset instrument	Change lamp Reset instrument	Change lamp Reset instrument			
7	00		Read Mn absorption	Read Ni absorption			
			solution B	solution B			
7	30	Read Sn absorption Read off calibration Read off calibration					
		Read Sn absorption solution A					
8	00	Read off calibration					
9	00						
9	30	-	Pb% Mn% Fe% Ni%				
<u> </u>		Al% Sn%					

In this context the application of the more sophisticated instrumentation could be of interest.

Using a double channel instrument, it is possible to obtain a ratio measurement of the absorption of two elements in the same solution. A solution of brass, for example, can be analysed for both zinc and copper simultaneously and a ratio of their absorbance read out.

Many minor volumetric errors and variations in the nebulizer-flame system should be corrected. Some results obtained by this technique are given in Table 9 for the analysis by brasses for copper content. No particular care was taken in the dilution stages and indeed a deliberate error of 1.5% was made in one weighing of the No. 5 sample. The results show a very high reproducibility and an acceptable accuracy (24).

TABLE 9. Application of double beam, double channel atomic absorption to the determination of copper in brasses.

(a) Accuracy

	A.A.S.	. Results	Chemical	
Sample	Day 1 Cu (%)	Day 2 Cu (%)	(electrolytic) Cu content (%)	
1	51.4(7)	51.2(8)	51.37	
4	55.09	55.0(6)	55.20	
6		65.1(0)	65.14	
29	71.58	71.4(4)	71.48	
5	60.24	60.6(2)	60.46	

(b) Precision

Sample	Number of			Coefficient of
Sample	Weighings	Aliquots	Reading	variation (%)
60/40 St	1	1	10	0.1
29	1	1	11	0.1
1	1	1	11	0.23
5	4	4	8	0.26
	1	1	5	0.2
	1	4	20	0.3

DATA TREATMENT

The advent of cheap computer systems has resulted in most of the equipment, currently being installed in control laboratories, being fully computer controlled. The selection of the appropriate programme by the operator will thus initiate via the computer:-

- (a) The selection of the spectral lines.
- (b) The source conditions or primary X-ray tube loadings.
- (c) Analytical times.
- (d) Store results.
- (e) Compare with stored calibration data.
- (f) Correct for inter-element effects.
- (g) Print out directly in concentration terms.
- (h) Compute remedial additions to the charge.
- (i) Monitor and report on instrument malfunction.

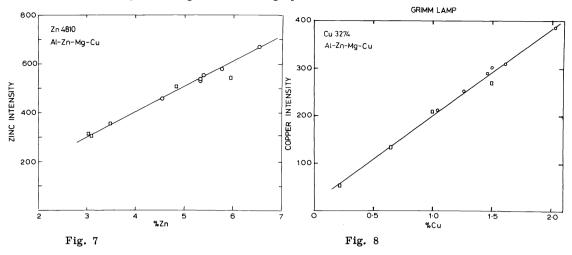
Operator error is thus reduced to a minimum.

R&D IN NON-FERROUS ANALYSIS

With the industries' analytical requirements being largely satisfied, particularly in the process control area, by the physical instrumentation currently available, R&D work into analysis is concentrated into a narrow area. This is mainly the extension of analytical techniques into lower concentration areas, since interest in purer base metals is increasing.

However, the use of the Grimm Lamp source in optical emission is being studied, particularly for its low background characteristics and the alleviation of inter-element effects.

Figures 7 and 8 demonstrate this for zinc and copper in a series of aluminium alloys where, with conventional excitation, a meaningful calibration graph could not be drawn(25).



Atomic fluorescence analysis, which initially promised much, particularly in the area of trace analysis, has not had the impact expected of it, largely, it is suspected, because of the lack of commercial instrumentation. That it could be a useful tool is shown in Table 10, where the technique has been applied to the analysis of copper for tellurium and selenium at the ppm level. Linear calibration curves were obtained over the range 0.0001-0.0012% of both elements, with standard deviations at the 0.0004% level for tellurium of 0.00004% and selenium of $0.00002\%^{(26)}$.

TABLE 10. Atomic fluoresence analysis of copper.

G 1	Tellurium (%)		Selenium (%)	
Sample	Chemical	AFS	Chemical	AFS
A	0.000(1) 0.000(1)	0.0003 0.0002 0.0003	0.0004 0.0005	0.0003 0.0003 0.0003(5)
В	0.000(1) 0.000(2)	0.0003 0.0002 0.0002	0.0002 0.0002	0.0002 0.0002
С	0.000(05) 0.000(1)	0.0003 0.0003 0.0004	0.00025 0.0003	0.0003 0.0003 0.0002

The high sensitivities obtainable by the non-flame, mainly carbon tube, atomisers in atomic absorption may have influenced the swing in interest away from the fluoresence mode. The introduction of the carbon tube atomiser into the analytical R&D laboratories in the industries is quite recent and little concrete information is available.

However, some very preliminary $work^{(27)}$ into its application to the analysis of copper, the results of which are shown in Table 11, suggests the technique should have wide application in the analysis of the pure and ultra-pure metals.

The recent commercial availability of the inductively coupled plasma as a novel spectrometric source, with its wide concentration range of application, albeit mainly using solution samples, has invoked a lot of interest. It is to be hoped that the combination of this source coupled to a separate aerosol generator for solid metal samples (28) will be investigated as an integrated analysis system for control laboratories. It would seem that this approach could be an answer to the spectroscopists' desire to be able to separate and thus optimise the sampling and the excitation processes.

TABLE 11. Sensitivities of carbon tube atomiser in atomic absorption for pure copper.

Element	Wavelength n.m.	Limit of detection* (ppm)
Sn	300.9	0.4
Se	196.0	0.3
As	193.7	1.5
Fe	248.3	0.6

^{*50}g/1 solution 20 1 sample.

ENVIRONMENTAL PROTECTION

In common with most industrial countries more and more attention is being focussed on the impact of industry on the environment. Two recent pieces of legislation have accelerated the concern of industry (29,30). The Control of Pollution Act will require all industrial sites to inform the local authority of all the emissions from the site, which will then be available in a register open to public scrutiny. Water authorities, which control both the supply and discharge situations, have been given wider powers. The Alkali & Clean Air Inspectorate, which controls the emissions to air of certain registered industries, including large areas of the non-ferrous industry, has issued new regulations. In particular, these affect the aluminium industry and the lead industry, and the Inspectorate is in the process of defining new regulations for the copper industry.

These regulations have effect immediately on any new plant and it is estimated could involve extra capital expenditure of 25%. The Health & Safety at Work Act has focussed attention on the exposure of workers to toxic substances in air, particularly the heavy metals, lead and cadmium, where the threshold limit values for both have been reduced recently.

The analyst has a most important role to play in all this. He has a duty both to his employers and to the community at large to ensure that the analytical results, upon which the expensive remedial measurements largely depend, are both relevant and accurate. Much attention is then being given to the collection of the sample, for in this sphere, as in all others, the analysis can only be as good as the sample. All the analytical experience that has been gained with the techniques used in the analysis of the metal products will no doubt prove vital in this work which can be rightly called the growth area for analysis in the non-ferrous industries.

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