

THE ROLE OF ANALYTICAL CHEMISTRY IN THE FERROUS METAL INDUSTRY

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Abstract - In the ferrous metal industry analytical chemistry has always played a special role because of the economic importance of this industry. Nowadays, high speed analytical systems for the determination of multicomponent mixtures such as iron based alloys, ores or slags raise new problems. Therefore, this paper deals with the requirements of raw material analysis, process control methods, product analysis, and special analytical procedures or topological tests. It is divided into two parts: the state of development and unsolved problems.

INTRODUCTION

In the past the production of metals and analytical chemistry formed an indivisible unit. Approximately 400 years ago the alchemist who tried to produce gold had to test his products himself. Approximately 200 years ago C.W. Scheele (1742 - 1786) gave the following definition of chemistry: "Analysing substances into their components with skill, discovering their properties, and putting them together in different manners is the subject and the principle aim of the whole chemistry".

The analyst's skill was classified in the first place by the great philosopher I. Kant (1724 - 1804) and at that time was also able to fulfil his claim to show quantitative correlations by establishing their mathematics. The analytically proved stoichiometry made it possible for chemistry to be recognized as an exact science.

From this time analytical chemistry steadily lost its precedence and its reputation declined - but not its importance. Since the beginning of the era of industrialization analytical chemistry has gradually regained its status and today fulfils an important role.

It is small consolation that all essential technical developments of the 19th and 20th centuries came about with the help of analytical chemistry and the analyst's skill. Interpretation of the analyst's data was soon taken out of his hands although he could have done it best if he had been interested in the technological processes or the application of his data. This statement is obviously valid worldwide as emphasized by these words of H.A. Liebhafsky: "Like it or not, chemistry is going out of analytical chemistry".

My opinion is that analytical chemistry as a whole - sampling, data accumulation and processing - could have done much more for technological development as well as for establishing the nature and effects of such topics as environmental pollution.

Normally today the analyst's industrial service consists of the production of analytical data (sometimes called the Analytical Factory), and is, therefore, restricted to only two working steps of quantitative analysis (1): the sample preparation and determination methods. The analyst has to obtain innumerable results from samples of which he often knows neither origin nor history. These samples are often judged without knowing their actual origin. The analyst's know-how is often considered a nuisance and rarely used to the optimum. Today this view is widespread and its effect can be seen in training methods. The objective relations have always to be emphasized mainly for economic reasons. In the ferrous metal industry analytical chemistry has always played a special role because of its economic importance. Production of iron and steel entails the manufacturing of materials with very special properties which have normally

to be guaranteed. As a complete testing of these properties to a certain specification can only be carried out after production, or completion, a conclusion has to be drawn from knowing the chemical composition of the intermediate products about the quality of the final product during the production procedure. The determination of chemical composition is often useful for the analytical control of the final product, in the factory as well as with the customer because numerable correlations between composition or structure and material properties are known.

The task of analytical chemistry here is to analyse the composition of samples from liquid or solid iron and steel quickly and accurately.

When there was a sudden change in steel production processes in the direction of large charge units approximately 20 years ago, analytical chemistry achieved economic importance. Approximately 10 years ago this increased considerably with the increase of the charge-frequency and the beginning of automation so that the old analytical problem - speed and accuracy - had to be emphasized. As a result of the economic importance of preventing miss charges, money was available for the development of those methods which were in a position to give the required information within the shortest period. With these developments a renaissance of spectrochemical analysis took place and is still continuing. Therefore, spectrochemical methods have become characteristic of the high speed analysis of metals. It is obvious that the development of all spectroscopic methods had a great influence on the various different analytical problems which are connected with iron and steel production.

In modern laboratories analytical systems are used today which are a combination of classical and automated methods. With these it is possible to complete the establishment of the required data more quickly. High speed analysis has two substantial benefits, assuming the precision of the results remains valid:

1. the possibility of intervention in running processes, and
2. the saving of man-power, a cost reduction and the retrenchment of sample-waiting-lines.

The experience gained with the development of high speed systems for production control is at present used for the solution of additional analytical tasks. The analyst is forced to install large classical laboratories or to use the know-how of physical analysis (mainly spectroscopy) by the complicated requirements of new raw material contractors and different product specifications; and particularly by the need to deal systematically with ergonomic and environmental problems.

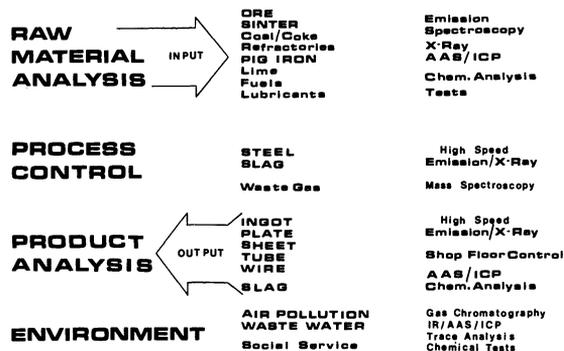


Fig. 1. Product-orientated methods of analytical chemistry

It is very difficult to classify the numerous tasks. This can be done according to the different classification principles, for example, according to the requirements, the necessities and the applied analytical methods. Placed above are 4 groups (Fig. 1): raw material analysis, production control, analysis of products, and environmental methods. This classification includes all groups

of substances which determine the kind and the speed of the analytical method to be applied.

When dealing with analytical problems in the iron and steel industry, organization within the laboratory is largely dictated by economic criteria. Normally it is impossible to install a central laboratory since the distances between the production plants and the laboratory must not exceed a certain transmitting time for samples which have to be treated quickly. Therefore, the co-operation between the different laboratory units is of importance too.

Quantitative analysis is shown in its most modern form in the ferrous metal industry:

The combination of electronics, physics and chemistry as well as every kind of management (planning, innovation and control) as a practical combined science.

This does not mean, however, that all analytical problems have been solved. It is only to show the way analysis has gone and has to go in the ferrous metal industry in future.

THE STATE OF DEVELOPMENT

Sampling. The very important sampling and sample preparation of bulk materials, ores, lime, coke or scrap (input) as well as every slag (output) is not dealt with here because the methods are already standardized.

The essential role of analytical chemistry in the iron and steel industry is high speed sampling and analysis during the production process. For the analyst it is imperative to know the procedure completely. Today the slowest step in the analytical procedure - sampling/analytical determination/data output - is sampling which requires approximately 2 - 3 minutes (or even more). Regarding this the development of better and more rapid methods started during the last few years.

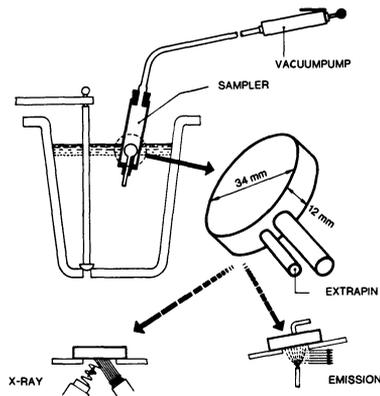


Fig. 2. Disc-pin sampling from a ladle containing steel

To date the result is an improved mechanism of sampling, for example, by combining temperature measuring in one container, and a change of the sample shape from the cone to the disc-pin sample which does not have to be cut (Fig.2). 1 - 2 minutes can be saved.

Apart from liquid steel sampling numerous samples of different kinds also have to be analysed with high speed techniques for economic reasons. The preparation of this routine sample has, therefore, to be controlled in such a way that this is possible. An essential facilitation of the preparation of metallic samples of different shape (chips, filings or powder) is the use of Rotomelt devices with which (by centrifugal casting after inductively heating in a ceramic crucible) samples can be produced which can easily be sparked or irradiated. The homogeneity of remelted samples is excellent because there is a complete dissolution of the typical structure of the material.

Generally the analytical results are only useful if the sampling is representative and remains constant in place, time and manner.

High speed spectrochemical analysis. The shop-samples are in fact never ideally homogeneous. On the sample surface area which is the actual sample covered by the method of analysis, some area per cent of non metallic inclusions with a length about the μ -level can occur. The object of development in emission spectrometry in analytical aspects of the ferrous industry was, therefore, to find universal sources which allow for reproducible results from ordinary samples too. Apart from that, the error in emission analysis allows the analyst to trace back 80% to the source while approximately 10% of mistakes are caused by electronics and approximately 10% by data processing. It is therefore explicable that the three significant types of sources were developed by industrial laboratories. There are the H.R.R.S. (high repetition rate source) of Höller (2) from Hüttenwerke Oberhausen AG (today: Thyssen Niederrhein AG), the H.E.P.S. of the laboratories of Hoesch Hüttenwerke AG, and the glow discharge lamp of Grimm (3) from Vacuumschmelze Hanau. The two first mentioned made their way into many laboratories of the iron and steel industry, and according to my findings our H.E.P.S. (4) is the most universal source today. High speed emission analysis with the glow discharge lamp which ought to be more universal on account of its conception can only be found in the I.S.C.O.R. laboratories of Radmacher (5).

So far, it is not generally necessary to remelt the samples totally, presuming that their shape is suitable for spectrochemical analysis. Progress in the direction of shorter sparking periods is significant (Fig. 3).

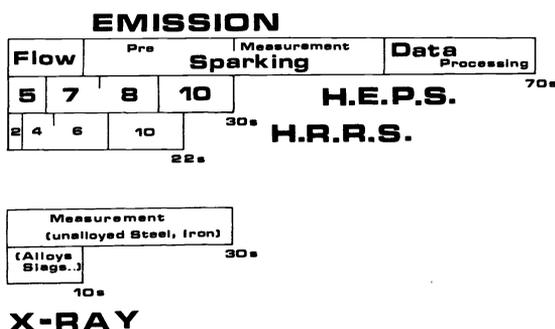


Fig. 3. Analytical times of high speed spectrometry

At the same time by limitation of the sparking spot a substantial remelting effect within the spot area arose (6). In a 20-year development emission spectrometry reached an optimum status regarding the speed and precision of the data. The combination spectrometer/computer gives a considerable contribution to this status; with which not only the electrical parameters of the source or detector systems can be controlled but above all both the systematic influences - the interelement effects and (sometimes) the coincidences of spectral lines can be eliminated mathematically. The supposition is that these effects, their sizes and directions are known.

Emission spectrometry is qualified for the high speed and precise determination of lateral components in a specific matrix. There is a great advantage in being able to determine carbon in one operation with the analysis of pig iron and unalloyed steels.

Besides this technique X-ray fluorescence spectrometry (XRF) made considerable progress during the last years. The XRF with a Rhodium tube of high power (3 kW) and a simultaneous measuring device has succeeded in a number of problems of routine analysis because the high precision of the results has been considered excellent for the determination of many elements (up to 30 at present) with high to relatively low concentration. Two important steps characterize the development of the simultaneous XRF: the arrangement of element monochromators in a great number around the sample and the fast data processing with all corrections.

Today in the laboratories of the ferrous metal industry times of analysis (Fig. 3) are reached which usually do not exceed 30 seconds for a single determination of 20 - 30 elements. The characteristic stamp of these analytical systems is the safety which guarantees a constant data flow. When analysing with high speed methods, in relation to the kind of material, the analytical operation between the arrival of the sample and the data print-out has also to be systematized. The spectrometer's efficiency, the improved knowledge about the analytical procedures and connections between actual sample, calibration or recalibration

and standardization of the methods led to a high precision (Fig. 4) of the results with extremely short measuring times. The standard deviation of many elements in the important concentration range is below 5%. There is no significant difference between the two principles except the higher concentration above 10% and the special case of sulphur with better XRF results.

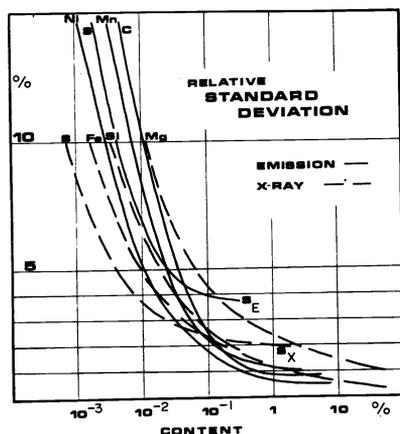


Fig. 4. Relative standard deviation as a function of the content using emission (————) and X-ray (-----) spectrometry

However, nothing is said about the accuracy of the results which is of decisive importance because of the producer's liability in the ferrous metal industry. Until today the use of accurate standard reference samples is an unsolved problem which has not been standardized. As there are no reference samples which were chosen according to spectrochemical aspects, the use of commercially obtained standards rarely brings accurate graphs. The most reliable way of plotting analytical functions for emission spectrometry is to use your own calibration samples in increasing amounts starting with two-base alloys as produced by ANALYTICA Sweden, for example. Preparing your own samples with the desired composition is possible by using the Rotomelt device. In this way interelement effects can be considered quantitatively and corrected accordingly. For plotting XRF analytical functions metallic samples of the same kind or, for oxides, mixtures of pure chemicals, if available, respective matrices with measured quantities of corresponding salts are used. In every case it is necessary to determine the "true value" with methods of chemical analysis.

Chemical analysis. Here too a change is evident as man-power becomes increasingly expensive. Naturally, chemical methods are necessary in addition to high speed routine analysis. Today there is an important development of classical methods as a result of the requirements of analytical control within and between the different laboratories to guarantee the accuracy of the results of the environmental and pollution control or the production of new special types of steel. From the requirements it can be seen that it is a question of 53 elements to date. Besides the time-consuming methods of gravimetry and volumetric analysis which are normally standardized first of all (ISO or EURONORM) spectrophotometric and electrometric methods appeared. From these the potentiometric indication of volumetric analysis which gives a document in the form of a potential curve and some methods of polarography because of their very high sensitivity for several elements, survived. For example, cathode radiation polarography has been approved for numerous elements e.g. As, Sb, Pb, Bi, Zn.

Of increasing importance is the accurate carbon and sulphur determination methods in the lower concentration range. It is impossible to compare analytical results from different laboratories because of differences in sample homogeneity and sampling technique. Explaining these difficulties in more detail would require an additional paper.

In addition to the classical spectrophotometric methods with specific reagents atomic absorption spectrometry (A.A.S.) has been increasingly successful. Nowadays we are analysing 26 elements from 16 different material groups by this technique. There is another considerable rationalization of chemical methods by using inductively coupled plasma (I.C.P.) emission spectrometry (7). The advantage of I.C.P. spectrometry in comparison with A.A.S. is based on the following facts: Simultaneous multielement analysis from one sample solution; complete dissociation of all compounds and ionization of all atoms; by

combination with efficient spectrometers the information of the emission spectrometry is fully utilized.

Here, however, in contrast with A.A.S., high resolution is necessary. This applies to the high sensitivity as well, as normally one can only operate with very diluted solutions. Nowadays we start with the determination of elements which cause difficulties with A.A.S., e.g. B, Nb, Zr, La, Ce, W and others. For this reason we are taking note of new methods and techniques. We shall test the application of I.C.P. emission spectrometry mainly with solutions of metallic or oxidic samples directly and the analysis of waste water as well as of gases after chemical reaction and, if possible, particle aerosols, e.g. after aerosol production by an arc source on metallic surfaces (8). An essential criterion in the laboratories of the iron and steel industry is the chemical control of spectrometry by means of several simultaneous analytical methods. A mean value, e.g. as a basis of calibration can be guaranteed best if at least two or more different analytical procedures produce corresponding results.

The increasing need for complete analytical information about the composition of many groups of new substances (input materials) has initiated a new development period of the old emission spectrographic method. Even today the information of the photo plate is unrivalled.

Table 1. Present methods of solution analysis used by the Hoesch laboratories

Analytical Method	Elements	Materials	Concentration/Range	Limit of Determination
Gravimetry	W, Nb, Zr, P, Si	Alloys Oxides	60 - 1 %	100 µg/g
Volumetry	Fe	Ores	65 - 50 %	
	Si Ca	FeSi Oxides	90 - 40 % 50 - 10 %	
Potentiometry	Mn, Cr, V Mo	Alloys Ferroalloys	60 - 5 %	100 µg/g
Polarography	Bi, Cu, Cd, Zn, As, Pb, Ag, Sb, Te ...	Steel Environment Water	0.1 - 10 ⁻⁵ %	0.1 µg/g
Gas Analysis	H, C, N, O, S	Steel/Iron Oxides	1 - 10 ⁻⁴ % (except carbon)	5 µg/g
Spectro- photometry	Al, Ce, Cr, Cu, Fe, Si, Ti, V, Mo, Nb, Zr, Mn, Co, S, Sn, P, F	Steel Oxides Water ...	10 - 10 ⁻³ %	1 µg/g
Atomic Absorption	Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cu, Fe, Ge, Li, Mg, Mn, Na, Ni, Pb, Sb, Si, Sn, Ti, V, W, Zn, Cr, Mo	Metals Alloys Oxides Water Lubricants...	10 - 10 ⁻⁴ %	0.1 µg/g
Flame Emission	Na, K, Li	Oxides Lubricants...	1 - 10 ⁻⁴ %	0.1 µg/g
Solution Emission	(70 Elements)	Lubricants Steel/Oxides Water...	10 - 10 ⁻³ %	1 µg/g
I.C.P. Emission	Al, B, Ca, Co, Cr, Cu, Ni, Pb, Nb, Si, Sn, Mn, Mo, Ti, Zn, Sb	Steel Oxides	10 - 10 ⁻⁵ %	0.1 µg/g
X-Ray	(50 Elements)	All Materials	10 - 10 ⁻³ %	1 µg/g

UNSOLVED ANALYTICAL PROBLEMS

There are always new variations in emission spectrography like the liquid-layer-on-solid-sample spark technique of Barnes (9) which is based on sparking through a permanently generated thin layer of water on a metallic sample surface. Characteristic of this method is a considerably large abrasion of material connected with higher intensities of numerous spectral lines.

We also modified the well-known rotating-disc technique for solution-spectrographic analysis in such a way that the sparking process takes place in an inert gas atmosphere. Normally many metals in analytical solutions like waste water or lubricants and gasoline can be determined without interference, e.g. CN-bands. Another example is the equipment of one of our simultaneously working XRF spectrometers with a scanner which can be adjusted to any element (from F upward) by computer impulse stepping. One can clearly recognize from the spectrum of "Ce-mischmetal" how small the number of lines is in comparison with emission spectrometry. There is normally no difficulty in selection of analytical lines. In this case (Fig. 5) it has to be considered that the L_{β} -line of La affects the L_{α} -line of Pr and likewise Ce/Nd.

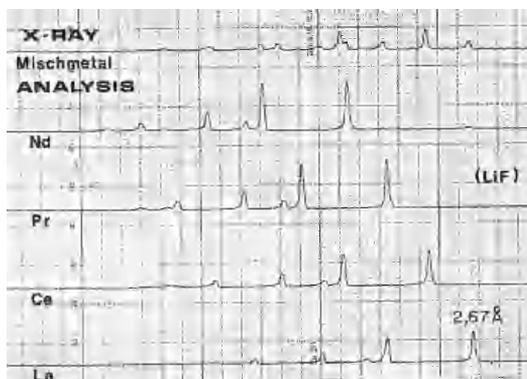


Fig. 5. X-Ray spectra of Ce-mischmetal; La, Ce, Pr and Nd between 2.0 and 2.7 Å (XRF spectrometer 72000)

XRF spectrometry is becoming the most important method - apart from I.C.P. emission spectrometry - of solving problems in the laboratories of the ferrous metal industry. Microanalysis can also be done with XRF. For this, small quantities of solution or solid are prepared on filter paper or in a plastic mould.

The actual microanalysis, for sample quantities below 1 mg, is carried out using special techniques of emission spectrography. The development of these methods in the Hoesch laboratory was subject to the size of the electrodes (Fig. 6) or the sample quantity which was available. Today we are able to determine from a weight of 10 µg, the main and if necessary oxidative by-products. This is possible by doing the melting fusion in a conic graphite crucible in such a way that a glass bead appears which can be vaporized and ionized by means of a laser-shot. The spectra resulting from these three techniques with different sample quantity input show that in every case nearly the same line intensities can be achieved. The relative standard deviation of approximately 3 - 5%, increases with decreasing weight to approximately 10 - 15%.

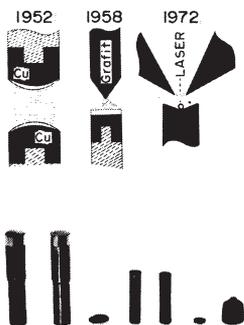


Fig. 6. Size of electrodes for spectrographic microanalysis

Trace analysis of analytical samples at the μg -quantity level is a completely unsolved problem. There have been no comparable results in this field from different laboratories up to the present time.

The problems become greater and less comprehensible as soon as one leaves the field of quantitative analysis. The analytical problems of the ferrous metal industry arise in the area where in some cases a quantitative value may be ascribed to a definite quantity, mass or volume, and where in other cases the precise values obtained cannot be ascribed to the bulk.

We have, for example, the analysis of residues which have been isolated from steel and which are difficult to classify but for which much information is required. Today one can receive information about composition and bonding out of very small sample quantities. Molecular spectroscopy plays a certain role in relation to bonding, for example, BN and Si_3N_4 which are found in steels as inclusions show typical infrared spectra.

The attenuated total reflection technique may be used for more than just the test for water. The quantitative determination of BN in the presence of SiO_2 in residues, can be done by reinforcing the BN-peak (11). The peak height ratios change with the BN concentration ratios in the sample.

With the application of the microprobe for determinations of inclusions in steel or concentration profiles we leave the field of quantitative analysis. The determination of substances on metallic surfaces should resort under topological analysis. Results are reported as "mass/surface area" ($\mu\text{g}/\text{cm}^2$).

In the Hoesch laboratory a very simple and sensitive method for the determination of substances on surfaces of steel sheets was elaborated with the XRF technique. The most important calibration is done with salt or acid solutions on the same area of clean steel plates. The direct measurement of substances on surfaces of thin sheets from production has to be followed by a background-correction (measurement after grinding). Many elements such as S, P, Cl, Si, Mn, Cu, Cr, Ni, Sn, Pb, etc. can be determined ($\mu\text{g}/\text{cm}^2$).

In connection with steels only a few applicable results are known and are determined by electron optical spectroscopy (ESCA, Auger, etc.) or ion optical spectroscopy. Correlations with the production process, e.g. in cold rolling mills, are not yet in existence.

A typical method for topological analysis is the application of laser emission spectrography. The craters in steel adapt to the problem with regard to diameter and depth (Fig. 7). The laser vapour ionizes a spark gap. Its emission enables the evaluation of numerous spectral lines after one shot. Much has still to be done in the field of topological analysis because the capacities do not correspond to the requirements.

Two other sections of increasing importance still belong to the hitherto completely unsolved problems, viz. inspection control in the shops and environmental analysis.

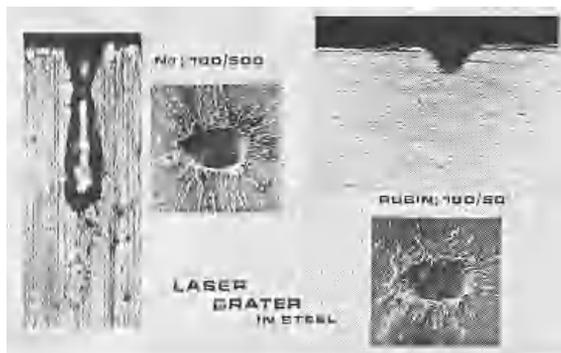


Fig. 7. Laser crater in steel, depth and diameter in μm

Shop floor control. One can already measure several guiding values during a steel production process, e.g. temperature, exhaust gas composition and also the free oxygen content of the steel bath by EMF-measurements as well as the calculation of dissolved Al from these data. The process-computer can obtain data from the composition of input materials and the product specification. Therefore, it will become possible in future that high speed analysis during the production process can be replaced by a more accurate analysis of the input

materials and the fast identification of the final products. However, as far as identification of today's products with their narrow limits of tolerance is concerned, highly sensitive spectrometric methods have to be applied.

There are numerous efforts in this field. Use of manual spectrosopes requires specialists and is restricted to only a few elements which are not always the most characteristic ones. This also applies to the non-dispersive methods with radiation sources.

Besides the determinations of single, typical elements there are more and more methods of simultaneous analysis of the complete composition, e.g. the production and transport of a complete metal aerosol or the transfer of light via glass fibre optics.

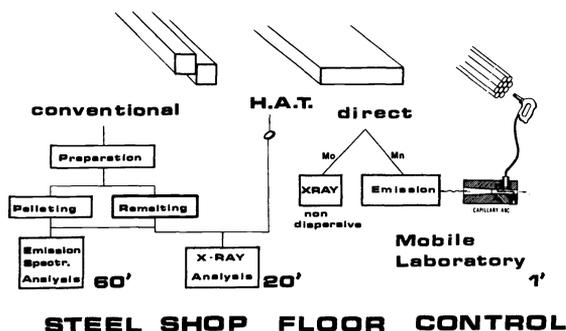


Fig. 8. Methods of inspection control

We developed in our laboratory the very simple Hoesch Abrasion Technique on hard alumina discs which can be applied to many metals, alloys and scrap identification (12). By means of the XRF one can analyse the thin film of metal on the alumina discs. Intensity ratios of count rates are used.

Environmental analysis. Pollution control and environmental analysis of solid, liquid and gaseous substances has been an unsolved analytical problem up to now. Apart from all the automatic measurements for air and water control, there is still a need for analytical chemistry. It is not possible to regard this problem as of secondary importance. At present it is sometimes impossible for chemical laboratories with optimized equipment and experienced staff to do all the determinations required by legislation. It has to be taken into consideration that time is a limiting factor and that trace analysis is practically always implied, often at the lowest level.

We have some precise analytical methods for these problems and new techniques are always being described. However, the main point is intercomparison of results with those of authorities and other laboratories.

By adjusting available working techniques the analysts are in many cases in the position to obtain reproducible values. However, nobody knows how accurate those are on the ppm-level and below.

Apart from the methods of analytical chemistry which are time-consuming but relatively accurate, increasing use is being made of techniques from which a great deal of information can be gained and hence costs are saved, for example, emission spectrography and XRF for dusts and oxidic residues, I.C.P.-emission spectrometry and A.A.S. for metals and waste water, and gas chromatography and infrared spectroscopy for gaseous samples.

A certain ambiguity is the real thread throughout our entire work: viz. the accurate calibration of methods for the various concentration levels. What is required is worldwide collaboration on standardized techniques so that analysts may at least speak the same language. The objective is: precision and accuracy.

CONCLUSION

High standards of speed and equipment are being attained in the laboratories of the ferrous metal industry. Both result in lowering of costs, but the degree of complexity has also increased. The analyst's qualifications have to keep pace with this. Analytical chemistry always leads to creativity in chemistry. The status of analytical chemistry in a country is an indication of its position as an industrialized nation and its chances in the future.

Table 2. Most important environmental elements from the point of view of the ferrous metal industry

Elements	Range of Concentration $\mu\text{g/g}$	Material (input)	Analytical Methods
As	0.1 - 2000	Iron ore	AAS/Polarography
Pb	1 - 1000	Iron ore	AAS/ICP-Emission
Zn	1 - 2000	Iron ore	AAS/Polarography
Cd	0.01 - 100	Iron ore	AAS/ICP/Polarogr.
Hg	0.001 - 10	Iron ore	AAS/ICP-Emission
S	2 - 20000	Fuels, Lime	Gas analysis (IR),
		Lubricants	Coulometry
Cl	1 - 5000	Water,	Volumetry,
		Oxides etc.	Polarography (Hg)
Se	0.1 - 100	Ores, Alloys	ICP-Emission
Te	0.1 - 200	Ores, Alloys	AAS/ICP-Emission
F	0.01 - 1000	Iron ores	Spectrophotometry,
			Ion sensitive electr.
Cu	0.1 - 10000	Scrap, Al-metal	AAS/ICP-Emission

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