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CURRENT APPLICATIONS OF SPECTROSCOPIC ANALYSIS (EMISSION, X-RAY FLUORESCENCE AND ATOMIC ABSORPTION) IN INDUSTRY AND RESEARCH IN THE UNITED KINGDOM

by

G. L. Mason*

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SYNOPSIS

This communication reports on a series of visits made to various industrial plants and research organisations in the United Kingdom during July and early August, 1967. The basic object of these visits was to obtain up-to-date information of current analytical applications of emission spectroscopy, covering as wide a field as possible, from minerals to metals. Further, since the allied techniques of X-ray fluorescence and atomic absorption could be covered just as easily at the same time, these were included in the survey. Also included in the itinerary, and reported herein, was an attendance at the Summer Conference of the Spectroscopy Group, held at Birmingham University on the 6th and 7th July. The theme of the Conference was "Accuracy of Spectroscopic Methods".

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Circulaire d'information IC 198

Direction des mines

APPLICATIONS ACTUELLES DE L'ANALYSE SPECTROSCOPIQUE (ÉMISSION, FLUORESCENCE AUX RAYONS X ET ABSORPTION ATOMIQUE) DANS LE DOMAINE DE L'INDUSTRIE ET DE LA RECHERCHE AU ROYAUME-UNI

par

G. L. Mason*

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RÉSUMÉ

Cette communication fait état d'une série de visites dans diverses entreprises industrielles et centres de recherches du Royaume-Uni en juillet et au début d'août 1967. Il s'agissait d'obtenir des données récentes en matière de spectroscopie d'émission, dans un domaine aussi vaste que possible, des minéraux aux métaux. Cette étude portait également sur les techniques connexes de la fluorescence aux rayons X et de l'absorption atomique, qu'il était facile de vérifier par la même occasion. L'itinéraire comprenait également la participation à la Conférence d'été des spécialistes en spectroscopie, dont un aperçu est donné dans la présente communication, qui s'est déroulée à l'université de Birmingham les 6 et 7 juillet 1967. Cette réunion avait pour thème "La précision des méthodes spectroscopiques".

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INTRODUCTION

Prior to coming to Canada, as a member of the staff of the Mineral Sciences Division, Mines Branch, the writer carried out a series of visits throughout industry and research in the United Kingdom, obtaining information of current analytical applications of emission spectroscopy. The final itinerary was arranged to cover as wide a field of application as possible (from minerals to metals) in the limited time available, and the opportunity was taken to include the allied techniques of X-ray fluorescence and atomic absorption in the survey. A total of twenty visits was completed during the period 3rd July to 1st August. The Summer Conference of the Spectroscopy Group (sponsored by the Institute of Physics and The Physical Society), held on 6th and 7th July at Birmingham University, was also attended. The theme of the Conference was "Accuracy of Spectroscopic Methods".

The itinerary of the visits is given in Appendix I. For purposes of classification, the reports on the separate visits are recorded herein under classified headings and not in chronological order. A brief summary of the Summer Conference, with comments, is presented in Appendix II.

ESTABLISHMENTS VISITED, EQUIPMENT AND APPLICATIONS

(a) Minerals and Mineral Dressing Products

1. D.S.I.R.I. Warren Springs Laboratories, Stevenage

The Analytical Chemistry Division is headed by Dr. P.G. Jeffery and provides analytical services (chemical, physico-chemical and physical) for the entire organisation, covering a wide range of minerals and mineral dressing products from all over the world. It was stressed at the commencement of the visit that, analysis-wise, the laboratory was not interested in determining concentrations of less than 0.01%.

A. Equipment

(i) Emission

1 Hilger large quartz/glass outfit	Both aligned to the same excitation stand.
1 Hilger medium quartz outfit	

(ii) X-ray Fluorescence

1 Philips 1212 automatic X.R.F. spectrometer

(iii) Atomic Absorption

1 Unicam SP90 with nitrous oxide/acetylene burner
1 " " " air/acetylene "

B. Applications

(i) Emission

This work has received no great attention and until recently a regular spectrographer had not been employed. Present application is limited almost entirely to the qualitative and semi-quantitative examination of powder samples, using a 15-amp D.C. arc and argon/air atmosphere with the Stallwood jet. Plate evaluation is carried out with the Hilger L99 comparator-densitometer.

(ii) X-ray Fluorescence

The PW1212 is applied to the analysis of a wide range of minerals, ores, dressing products and solvent extraction solutions. The common practice is to use the added internal standard technique, choosing the element next in atomic number to that sought (provided, of course, that no interference occurs and that the element is not present in significant quantity in the analysis samples).

With powder samples, borate fusions or pressings in lead rings are used to facilitate sample presentation.

(iii) Atomic Absorption

Methods are available (together with the appropriate lamps) for the determination of the following elements: Ag, Al, Au, Co, Cr, Cd, Cu, Fe, Mg, Mn, Mo, Ni, Sn, Pb, Si, Ti, and Zn. Lamps are also available for Ba and Tl, and work on these elements is proceeding.

Some 80 samples per day are analysed by atomic absorption and this technique, together with X-ray fluorescence, accounts for the majority of the analytical through-put.

A minor but interesting observation in connection with the application of the atomic absorption technique - the use of automatic diluting pipettes (the "Diluspence", supplied by Griffin and George Ltd.) giving dilutions of 1/5 and 1/100 was obviously a great time-saver.

(b) Zinc and Lead Smelting

2. Imperial Smelting Corporation Ltd., Avonmouth

The Chemistry Laboratory supervised by the Chief Chemist, Mr. G. Cosham, makes a wide use of optical emission and atomic absorption techniques, without which it could not possibly cope with the quantity and variety of analytical requirements of the plant.

A. Equipment

(i) Emission

1 A.R.L. "Standard Quantometer" fitted with tape machine
1 Hilger medium direct- reader (another on order)
2 Hilger medium quartz spectrographs

(ii) Atomic Absorption

1 Unicam SP90 with air/acetylene burner.
1 Experimental instrument designed around the Hilger "Uvispek" monochromator.

B. Applications

(i) Emission

The "Standard Quantometer" is used for the analysis of Zn alloys and Mazaks for the determination of the elements Pb, Cn, Fe, Mg, Al and Mn up to 0.5%, and Zn up to 5%. The excitation source used is the simple condensed spark; the 1/4"-dia. self-electrodes are in the form of spigot ends carefully machined and aligned.

The tape machine attachment is used in conjunction with a fusion/crushing technique (Co is added internal standard) for the determination of:

(a) Cu, FeO, MgO, SiO_2, Al_2O_3 and MgO in sinters;

(b) Pb, Cu, SiO_2, Al_2O_3, MnO, FeO, MgO, ZnO in smelting slags.

The Hilger medium direct-reader is applied solely to the analysis of Be-Cu alloys, determining the residuals Fe, Si, Co, Ni, Al, Zn, Mn, and the alloying element, Be circa 5%. The samples are in the form of cast discs, one face machined, and excitation is by the Hilger B.N.F. controlled source (capacity, 10 mfd; inductance, 0.015 micro-henry; residual resistance).

The medium spectrographs are applied daily to customer analysis (up to 84 pressure die-casting alloys per day), using the Kingsbury and McClelland intermittent arc source (48 mfd). Determination of the elements Al, Cu, Mg, Fe, Pb, Cd, Sn, In, Tl, Mn, Si, Ag, Si, Bi and Ga is carried out by visual appraisal against standard spectra recorded on the same plate.

The Jaycox oxide technique, using a 7-amp D.C. arc, is also applied to the examination of a wide range of residues and dressing products.

(ii) Atomic Absorption

This technique is applied on a large scale to the determination of the following elements:

Pb, Cd, ppm, to 20% in sinters

Zn, ppm, to 5% in liquors and residues

Cu, up to 20% in drosses

Na, ppm, in Zn metal and liquors

Ca, ppm, to 10% in liquors and sinters

Mg, ppm, to 1.0% in Mazak alloys

(c) High-purity Metals and Compounds

3. Johnson, Matthey and Co. Ltd., Wembley

Here the visit was confined solely to the Spectrographic Laboratory, supervised by Mr. D.J. Hobbs. No X-ray equipment is available.

A. Equipment

1 Hilger large quartz outfit
1 " medium " "
1 Ebert grating spectrograph equipped with new Universal Spex excitation stand
1 Hilger L99 comparator-densitometer
1 Hilger H451 densitometer, converted to multiplier-phototube read-out

Source units - 1 Hilger B.N.F.
1 newly-built controlled source (electronically triggered) to own design.

B. Applications

The D.C. arc source, in conjunction with the Stallwood jet incorporating an argen-oxygen atmosphere, is applied to the examination of a wide range of high-purity metals and compounds, for element concentrations down to 10^{-9}.

In view of the great number of element concentrations of this magnitude with which the laboratory has to deal, considerable use is made of the principles detailed in a recent paper by Hobbs and Smith*, developed to cope with determinations of this "region of uncertain detectability" (or "r.u.d." as Hobbs refers to it). Because of the amount of time involved in the assessment of the replicate spectra (21 for each sample) required by this method of analysis, there is a considerable delay in completion of analyses, and serious consideration is being given to the acceleration of this process by:

(i) the modification of the present motor-driven H451 densitometer to provide faster scanning over the entire spectrum plate and coupled to a suitably modified millivolt chart recorder.

(ii) the use of an Olivetti Programmer 101 'computer' to interpret the intensity measurements obtained by (i).

The Ebert grating instrument is applied solely to the examination of rare earths.

(d) Semiconductors and Allied Materials

4. Mullard Radio Valve Co. Ltd., Mitcham

The analytical laboratories of this Company, under the guidance of the Chief Chemist, Mr. C.R. Gentry, have been outstanding in their contributions to the development of spectrochemical methods. However, some 12 months ago the decision was made, in the light of the Company's present requirements, to discontinue development work and be concerned solely with the quality-control requirements of production. Each analytical problem is considered on its individual merits before the decision is made as to the analytical technique to be applied. In many instances the sample for analysis may be only a few milligrams or less in weight.

Semiconductors as such are no longer analysed, but a strict quality-control check is observed on all incoming raw materials.

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*The Evaluation and Application of the "Limit of Detection" in Quantitative Spectrographic Analysis, D.J. Hobbs and D.M. Smith; Canadian Spectroscopy, Vol. II, No. 1, January 1966.

A. Equipment

1 Hilger large quartz outfit
1 " medium " "
1 " B.N.F. source unit

Hilger 451 densitometer converted to multiplier-phototube measurement with 0-100 micro-ammeter

Respectra calculator

Special excitation sources - (a) hollow cathode
(b) Oldfield's argon/oxygen-atmosphere arc

(ii) X-ray Fluorescence

Philips PW1540 Vacuum X.R.F. outfit with P.H.A.;
PE and LiF crystals

(iii) Atomic Absorption

Hilger atomic absorption spectrometer - modified by Mullard's to give greater sensitivity

B. Applications

(i) Emission

The majority of optical emission analysis is carried out using the two special sources (hollow cathode and D.C. arc in argon/oxygen atmosphere) which are applied to the quantitative examination of oxide films and coatings, etc., occurring in valve components. The general practice adopted is that of removal in the minimum amount of mineral acid (transistor grade) and evaporation onto a pre-formed graphite electrode (Ringsdorff RWO544) with counter electrode (FWC085).

(ii) X-ray Fluorescence

The X-ray fluorescence technique is applied largely to the following analytical problems:

(a) determination of the concentration ratios of Ba, Sr and Ca in carbonate mixtures for anode manufacture, utilising a solution technique;

(b) determination of Zn in Ni: the Zn is separated from a HNO_3 solution by the addition of an Fe salt and ammonia; the precipitated Fe carrying the Zn with it is filtered onto a glass fibre disc and irradiated in situ;

(c) determination of S in oils;

(d) analysis of stainless steels;

(e) determination of Pb (0.01-0.20%) in leaded steels;

(f) analysis of brass and bronze when required for special check purposes.

(iii) Atomic Absorption

Used for the determination of very small amounts of Mg.

5. Mullard Research Laboratories, Salfords

Unlike the laboratories visited at Mitcham, the Research Laboratories do not provide routine analytical services as such. Because of the tremendous amount of research and development proceeding at Salfords in connection with solid state physics, and because of the highly specialised nature of the associated materials, the Analytical Division under the direction of Mr. E. Millett freely undertakes expensive research into complex analytical problems, the actual expense in truth being relatively cheap in the end-point, compared with the cost of the materials under examination. These materials range through thin films, magnetic storage elements, rare earth mixtures, to single-crystal materials (e.g. germanium arsenide epitaxies).

A. Equipment

(i) Emission

1 Hilger large quartz outfit equipped with separate D.C. arc, spark and source excitation

(ii) X-ray Fluorescence

1 Philips PW1210 X.R.F. outfit

(iii) Mass Spectrometry

1 A.E.I. M.S. 7 mass spectrometer

(iv) Atomic Absorption

1 atomic absorption spectrometer combining a Jarrell-Ash monochromator with "Techtron" electronics and lamps.

B. Applications

(i) Emission

The quartz spectrograph is used mainly as a qualitative and semi-quantitative sorting tool and for day-to-day ad hoc materials examination. The analytical techniques applied vary with the nature of the materials handled and cover powders, metal foils, wires, rods, solutions, etc.

(ii) X-ray Fluorescence

The Philips PW1210 is used for the analysis of thin films (80/20 Ni/Fe alloys) and magnetic storage elements, also for the determination of Ce(s.d. of ± 0.10% Ce at 60% level), Fe, and Zn.

(iii) Mass Spectrometry

The MS7 is utilised for critical analyses of single-crystal materials, e.g. germanium arsenide epitaxies, both in wafer form and in 1 mm-square-section rods pressed from the ground material mixed with graphite. The mixture is pressed in a special die at 4 tons on the plunger (40 tons/sq. in.).

(iv) Atomic Absorption

This technique is applied to the determination of small amounts of Ca, Cd, Zn, Al, Al, Mn, Ir and Nd in various materials.

(e) Radioactive Materials

6. U.K. Atomic Energy Research Establishment, Harwell

Unfortunately, this visit was made just after the Analytical Services Division (headed by Dr. A.A. Smales) had moved into a new Laboratory building, and little or no work was in progress.

Practically all analytical problems are associated with the minimum amount of sample (e.g. 0.05 mg of stabiliser strip), and the materials analysed range from radioactive liquors and residues to corrosion products, even clinical investigations (e.g., sheep's eyes, urine, and excreta).

Equipment

(i) Emission

6 Hilger large quartz outfits
4 " medium " "
1 3-metre Jarrell-Ash grating spectrograph
1 3-metre Hilger grating spectrograph
1 Ebert instrument
2 Hilger L99 comparator-densitometers

Excitation sources - 7-amp D.C. arc, copper spark, plasma jet and Jarrell-Ash laser beam are also used.

(ii) Atomic Absorption

1 spectrometer designed around the Hilger Uvispek monochromator
1 "Techtron" spectrometer

(iii) Flame Photometry

2 flame photometers designed around the "Uvispek" monochromator

(iv) Gases in Metals

1 vacuum spectrometer for the automatic determination of O_2, H_2 and N_2 in metals

Applications

(i) Emission

The majority of emission work is carried out using the 7-amp D.C. arc as excitation source. Use is also made of the copper spark where sensitivity and minimum sample (0.05 ml solution) go hand in hand. Work will be proceeding with the plasma jet and laser beam which as yet are relatively untried sources in the U.K.

(ii) Atomic Absorption and (iii) Flame Photometry

Little information available except that (iii) is used mainly for determination of the alkali metals, in parts per million.

(iv) Gases in Metals

The reported work of M. S. W. and R. J. Webb in applying the use of a high-temperature, hollow-cathode discharge for the determination of oxygen in steel has now been extended to include N_2 and O_2 in steel and uranium carbide, O_2 in W and Cu, and H_2 in Zr and its alloys.

A feature of these Harwell spectrographic laboratories is the provision of separate laboratories and equipment for the various applications; e.g., the determination of Be(by the large quartz) was carried out in one laboratory, and the analysis of radioactive materials in another, with separate laboratories for the plasma arc, laser, atomic absorption, and flame photometry.

(f) Non-Ferrous Metals and Alloys

7. International Nickel Research Laboratories, Birmingham

The laboratory visited is supervised by Mr. K. Bills and utilises emission and X-ray fluorescence spectrography, mass spectrometry and atomic absorption techniques in the examination of a wide range of materials connected with the application of Ni in Ni-, Cu-, Fe- and Cr-base alloys and "Nimonics".

A. Equipment

(i) Emission

1 Hilger large quartz/glass outfit
1 " " quartz outfit
1 Ebert grating spectrograph
1 H451 densitometer with motor drive
1 Hilger 90 comparator-densitometer

(ii) X-ray Fluorescence

1 Solartron automatic X.R.F. spectrometer from which the flow proportional counter has been discarded.

(iii) Mass Spectrometry

1 A.E.I. MS7 mass spectrometer

(iv) Atomic Absorption

1 atomic absorption spectrometer designed around the Hilger "Uvispek" monochromator, with air/acetylene and nitrous oxide burners.

B. Applications

(i) Emission

Emission techniques are used for the determination of the normal impurity and addition elements in Ni-, Cu-, Fe- and Cr-base alloys over the composition range 0.5 ppm to 5%.

(a) D.C. arc excitation is used in conjunction with the large quartz/glass instrument and the Jaycox oxide technique for the determination of trace elements. The oxide sample is mixed 1:1 with Ringsdorf RWO grade graphite powder and packed in pre-formed RWO crater electrodes 1/8" internal dia.

Arc conditions: Arc current, 5 amps; arc gap, 4 mm.
Exposure: 40 seconds on Ilford N20 plate,
using 2-step rhodium filter.

(b) Spark excitation - is used in conjunction with the large quartz instrument for the determination of elements generally in the concentration range 0.10 to 5.0% in solid samples.

Spark conditions: 15KV, 005 mfd, residual resistance,
supplied from Hilger B.N.F. source.

(c) Ebert grating spectrograph employed on a limited scale only for the determination of tellurium in "Nimonics".

(ii) X-ray Fluorescence

The Solartron instrument is applied to the analysis of Ni, Cu, Fe and Cr base alloys and "Nimonics" for the determination of all the usual elements above atomic number 21 from 0.01 to 100%. A solid sample technique is applied throughout, using short-range calibrations requiring a considerable number of standard samples.

The LiF crystal and the scintillation counter are utilised in each case and no interference or matrix corrections are required. The instrumental limitations of the Solartron have precluded its application to the lighter elements below atomic number 22.

The purchase of a modern automatic spectrometer is now receiving serious consideration.

(iii) Mass Spectrometry

The MS7 is used for the detection of trace impurities in metals, alloys and ferro-alloys, also in all materials used in the production of "Nimonics". Within a short while of its commissioning the instrument had proved itself invaluable in discovering hitherto unsuspected low-level impurities (down to 0.001 ppm) in both electrolytic and Mond nickel.

(iv) Atomic Absorption

Initial investigations are exploring the possibility of the determination of Al and Mg in "Nimonics".

8. Imperial Metal Industries (Kynoch) Ltd., Research and Routine Laboratories, Witton, Birmingham

The above laboratories are headed by Mr. W. T. Elwell, whose contributions to the development of both chemical and physico-chemical methods of analysis are recorded in several text-books which have received world-wide circulation.

I. Research Laboratories

A. Equipment

(i) Emission

1 Hilger large quartz outfit
2 " medium " outfits
1 Ebert spectrograph
B.N.F. and D.C. arc source units

(ii) Atomic Absorption

1 Perkin-Elmer atomic absorption spectrometer
1 laboratory-built instrument designed around the Hilger "Uvispek" monochromator

B. Applications

(i) Emission

The large quartz instrument can be used when required (on a quantitative and semi-quantitative basis) for the determination of:

(a) Al, Cr, Co, Cu, Fe, Mg, Mn, Mo, Ni, Pd, Si, Sn, W, V and Zr in Ti and its alloy

(b) Al, Cd, Cr, Co, Cu, Hf, Fe, Pb, Mg, Mn, Mo, Ni, Nb, Si, Sn, Ti, W, and V in Zr alloys

(c) Al, Ca, Cr, Co, Cu, Fe, Mg, Mn, Mo, Ni, Nb, Si, Ti, W and V in Hf

(Methods a, b and c utilise a point-to-plane technique and controlled excitation from the B.N.F. source unit.)

(d) Al, Ca, Mg, Ni and Ti in Hf

(e) Al, Cr, Hf, Fe, Mg, Mn, Mo, Ni, Si, Ta, Ti, W, V and Zr in reactor grade Nb

(Both methods d and e utilise the oxide-resin technique with controlled excitation from the B.N.F. source unit.)

(f) B, Cd and Pb in Zr, and B, Cd, Sn in Nb, by carrier-distillation technique using the simple D.C. arc

(g) trace impurities in Cu and Cu-base alloys, by the oxide technique and D.C. arc excitation

(h) La, Ce, Pr, Nd, Sm, Eu and Gd in Zr, employing high-voltage condensed spark excitation

The medium quartz spectrographs are used for the determination (quantitative or semi-quantitative) of:

(j) Zr(up to 4%) in hafnium alloys by means of the point-to-plane technique with high-voltage condensed spark excitation

The Ebert spectrograph has a limited application for the determination of Ca (up to 100 ppm) in Zr, using the oxide-resin technique together with controlled-arc excitation from the B.N.F. source unit.

(ii) Atomic Absorption

It is the laboratory policy to carry out as much analytical work as possible with this technique.

The two spectrometers are used to determine:

Co up to 4% in Cu-base alloys

Pb " " 5% " " "

Ag " " 0.2% in Cu and Cu-base alloys

Zn " " 5% in Cu-base alloys, up to 1% in Ti and its alloys,
and up to 200 ppm in Zr

Mg up to 200 ppm in Ti and its alloys

Na " " " " " " " " " and in Zr and its alloys

Ca " " 30 ppm in Zr, Hf and their alloys

Cu " " 0.50% " ", " " " "

II. Rod Mill Laboratory

As the name implies, this laboratory is situated close to the Rod Mill and supplies all the analytical requirements for routine production control on a 24-hour basis. Analysis samples are transported by means of a pneumatic Lamson tube system.

A. Equipment

(i) Emission

2 Hilger medium quartz outfits
1 Hilger 3-metre "Polychromator" D.R. spectrometer
1 A.R.L. "Uvaq" air-path/vacuum D.R. spectrometer,
28 element/40 channel programme, newly installed
and not then commissioned

(ii) X-ray Fluorescence

1 Solartron automatic X.R.F. spectrometer from which the flow proportional counter had been discarded.

B. Applications

(i) Emission

The medium spectrographs are used for the determination of the usual trace impurities in a wide range of alloys, utilising both solid-sample and globule-arc techniques.

The 3-metre "Polychromator" determines Al and Si in brass and bronze; also impurities down to 0.01% when required. When the Uvac spectrometer is finally commissioned this instrument will be expected to take over the whole of the work at present carried out with the two medium quartz spectrographs.

(ii) X-ray Fluorescence

The Solartron X.R.F. spectrometer is applied to the production control analysis in brass founding, determining the main alloying elements (excluding Al and Si). On the occasions when the instrument goes out of commission, the Hilger "Polychromator" is substituted. In common with the experience gained with the Solartron at Imperial Metal Industries, it has been found impossible to determine the lighter elements below atomic number 22.

III. Titanium Laboratory

Situated in the same building as the Rod Mill Laboratory, this laboratory houses a recently acquired Philips 1220 fully automatic X.R.F. spectrometer, and the development work now proceeding will, it is believed, permit the successful determination of up to 24 elements in Ti- and Zr-base alloys.

Present work has been confined mainly to trials with a solution technique, utilising HF/HCl and water as a solvent. Calibration graphs so obtained have proved remarkably linear, with a maximum counting time of 200 seconds. It is hoped to replace shortly the solution technique with a solid-sample method in which the requisite discs will be punched out by hydraulic means.

IV. Sheet and Wire Laboratory

Housed within the Sheet and Wire Mill, this laboratory provides all the analytical requirements of routine production control.

A. Equipment

(i) Emission

2 Hilger medium (12-channel) D.R. spectrometers

(ii) X-ray Fluorescence

1 Solartron X.R.F. spectrometer identical to that installed in the Rod Mill.

B. Applications

(i) Emission

The 2 direct-readers carry out impurity analyses on all finished materials.

(ii) X-ray Fluorescence

The Solartron spectrometer is used for the routine determination of all the usual alloying elements (except Al and Si) in brasses and bronzes, on a 24-hour, 3-shift basis.

9. Henry Wiggin and Co. Ltd., Hereford

A subsidiary of International Nickel Ltd., their laboratories are supervised by Chief Chemist Mr. E. Balfour with Mr. D. Jukes, Chief Spectrographer.

A. Equipment

(i) Emission

3 Hilger large quartz outfits
1 " medium " outfit
1 Hilger 3-metre "Polychromator" D.R. spectrometer
1 Ebert spectrograph

(ii) X-ray Fluorescence

1 Philips PW1009 air-path X.R.F. spectrometer
1 " PW1212 fully automatic X.R.F. spectrometer

(iii) Atomic Absorption

1 Hilger "Uvispek" with atomic absorption attachment

B. Application

(i) Emission

One large quartz outfit is applied entirely to development work - at present investigating the hollow cathode technique. The remaining large quartz and the medium outfits are applied on a routine basis to the determination of impurities in Ni-base and Cu/Ni alloys. According to the material, the methods vary from globule arc, powders, to solid metal techniques utilising D.C. arc or condensed spark excitation as required.

The Hilger "Polychromator", prior to the commissioning of the Philips PW1212, was applied on a routine shift basis to the analytical requirements of production control (bath sampling) and for the analysis of finished materials. It is now used only rarely, acting mainly as a stand-by in the event of the PW1212's becoming unserviceable.

(ii) X-ray Fluorescence

The Philips PW1212 spectrometer is operated on a 24-hour basis throughout a 5-day week for the analysis of bath samples and finished materials (Ni-base and Cu/Ni alloys). Both solid samples and powders are analysed; no solution or pellet samples have yet been examined.

The older PW1009 spectrometer is used only for the determination of Cu/Ni and Fe/Ni ratios in solid samples.

(iii) Atomic Absorption

As yet, this technique is applied solely to the determination of Mg in a wide range of materials, the concentration range covered being 1 ppm to 0.10%.

10. Yorkshire Imperial Metals Ltd., Leeds

The development and application of spectrochemical techniques at Y.I.M. are the responsibility of the Company Spectrographer, Mr. J. Cross, who also oversees the direct-reading spectrometric developments at their Kirkby (Liverpool) works.

A. Equipment at Leeds Works

(i) Emission

2 A.R.L. 1.5-metre grating spectrographs
1 " high-precision source unit
1 B.N.F.-type source unit
2 A.R.L. comparator-densitometers

(ii) X-ray Fluorescence

1 Solartron fully automatic X.R.F. spectrometer with flow proportional counter discarded

B. Applications

(i) Emission

The 2 A.R.L. spectrographs are applied on a 24-hour, 3-shift basis to the semi-quantitative determination of the normal range of impurities experienced in copper and copper-base alloys; also to the quantitative determination of Al and Si in a wide range of brasses and bronzes. Both D.C. arc and controlled-source excitation are used.

(ii) X-ray Fluorescence

The Solartron spectrometer also operates on a 24-hour basis, providing the routine production control analysis of brasses and bronzes for the major and alloying elements above atomic number 21.

Analytical Ranges	%Cu
Cu in brass	55-100
" " Cu/Ni	30-100
" " Brass (containing 1%Sn, 2%Pb)	Around 60%
" " Cu-Al	88-100

also Sn up to 12%, Pb up to 11% and Ni up to 40%. Close group calibrations, using a large number of standard samples, are employed.

Typical correction applied in the determination of Ni in Cu/ Ni:

$$\mathrm{Ni}_{\mathrm{true}} = \mathrm{Ni}_{\mathrm{obs.}} + K \left[(\mathrm{Fe} - \text{background}) + (\mathrm{Mn} - \text{background}) \right],$$

where K = 1/ 2 at 5%Ni,

1 at 10%Ni,

2 at 30%Ni,

2.6 at 70%Ni.

(iii) Direct-reading Developments at Kirkby Works

Two years ago, on the strength of experience gained at Leeds, an A.R.L. "Uvaq" (air/ vacuum) spectrometer was installed at Kirkby for the direct-reading determination of impurities in copper. Although considerable success has been achieved in this particular application, experience indicates that at the moment there are many difficulties to be overcome (interference and matrix effects) before such an instrument can be applied successfully to the analysis of brasses and bronzes. Details of the analytical specification of the Kirkby instrument are given below:

Element b'ground	Wave-length, A°	Air or Vacuum Line	Receiving Slit Width (microns)	Line= b'ground at ? %	Analytical Range,%
P	1782.7	Vacuum	50	0.008	0- 0.15
Fe	2739.5	Air	75	0.021	0- 0.10
S	1807.3	Vacuum	50	0.004	0- 0.06
As	1972.0	"	50	0.046	0- 0.20
Sb*	2068.0	"	75	0.135	0- 0.10
Zn	3345.0 x 2	Air	"	0.094	0- 0.20
Cd	2144.4 x 3	"	"	0.005	0- 0.05
Mn	2933.0	"	"	0.023	0- 0.12
Al	3961.5 x 2	"	"	0.010	0- 0.20

*High background.

(Cont'd) -

(Cont'd) -

Element	Wave-length, A°	Air or Vacuum Line	Receiving slit width (microns)	Line= b'ground at ? %	Analytical Range,%
Mg	2795.5	Air	75	0.001	0 - 0.05
Cr	2677.2	"	"	0.05	0 - 0.07
Si	2881.6 x 2	"	"	0.024	0 - 0.10
Sn	1899.0	Vacuum	50	0.005	0 - 0.15
Pb	2833.1 x 2	Air	75	0.094	0 - 0.10
Ni	3414.8 x 2	"	"	0.08	0 - 0.13
Bi*	3067.7 x 2	"	"	0.0198	0 - 0.01
Ag	3382.9	"	"	0.022	0 - 0.10
Co	3453.5 x 2	"	"	0.055	0 - 0.20
Te*	2142.7	Vacuum	50	0.175	0 - 0.04
Se	1960.9	"	75	0.015	0 - 0.20
Zr	3438.2	Air	"	0.013	0 - 0.15
Be	3131.1	"	"	Not yet applied	
B**	2496.8 x 2	"	50	0.01	0 - 0.20
C**	1930.9	Vacuum	"	0.01	0 - 0.10
Hg*	2536.6	Air	75	Not yet applied	
B'ground***	2008.56	"	"		
B'ground***	2008.54	Vacuum	50		

*High background. **In Cu/Ni alloys. ***Internal Standard.

Source Conditions:

C, 22 mfd; R, 16 ohms; L, 360 micro-henries. 60° pointed Cu counter electrode. Exposure (in sec.): Argon pre-flush, 10.
Pre-burn, 20.
Integration (vac), 30
" (air), 40

All graphs are linear over the quoted ranges

Read-out: 1 digit = 0.001%

Overall standard deviation of the method = 0.001%

C.V. ± 10%

11. British Non-Ferrous Metals Research Association, Euston, London

In the B.N.F.M.R.A. laboratories the physico-chemical analytical services are headed by Dr. Reynolds, the spectrochemistry section being supervised by Mr. English.

A. Equipment

(i) Emission

1 Hilger large quartz outfit
1 " medium " "
1 A.R.L. "Quantometer"

(ii) X-ray Fluorescence

1 air-path Solartron X.R.F. spectrometer
1 Telsec "Betaprobe"

B. Application

(i) Emission

(a) The large quartz instrument is set up for use with the hollow cathode source where extreme accuracy is required at very low trace levels. The medium quartz is applied to the determination of trace impurities in a wide range of Al-base and Cu-base alloys, by the globule arc technique, and to the determination of the lower concentrations of alloying elements in the same materials, using high-voltage condensed spark excitation.

(b) The "Quantometer" is applied to the determination of impurities and alloying elements in Al-base and Cu-base alloys.

(ii) X-ray Fluorescence

The Solartron spectrometer is applied to the major constituents in Al- and Cu-base alloys (from Ti upwards in the order of atomic number).

The Telsec "Betaprobe" is a recent acquisition which utilises electron beam excitation and is designed as a 6-channel, fixed-programme instrument for the determination of the light elements Al, Ca, Si, Mg, S, and P. At the time of the visit, long-term tests were in progress to observe the stability and reproducibility of the instrument. It is hoped to apply it to the determination of the above elements in Cu-base and Zn-base alloys and Ca, Si, Mg, S and P in Al-base alloys. By reason of its excitation source the instrument is remarkably sensitive, but its fixed programme renders it completely inflexible and so limits its field of application. As a research tool it promises very little in its present form.

(g) Ferro-Alloys

12. London-Scandinavian Metallurgical Co., Rotherham

London Scandinavian is a small works specialising in the production of ferro-alloys for industry. Until the setting-up of the existing spectrographic laboratory all analysis was done by wet chemistry, involving in many cases long and tedious separations. The enthusiasm for spectrochemical techniques, shared by both Chief Chemist Mr. G. Holmes and Spectrographer Mr. L. Giles, has during the past two years revolutionised the analytical services to the extent that the majority of routine analyses are now carried out by means of spectrochemical techniques, both by emission and X-ray fluorescence.

A. Equipment

(i) Emission

2 Hilger large quartz outfits
1 Hilger L90 comparator-densitometer

(ii) X-ray Fluorescence

1 Philips 1210 semi-automatic X.R.F. spectrometer, modified by suitable switching to provide an almost fully automatic instrument

B. Applications

(i) Emission

The two large quartz instruments are used for ad hoc preliminary examinations (quantitative and semi-quantitative) of a range of ores and ferro-alloys by the powder, arc, spark and solution techniques. Upon the results of these determinations depends the choice of the final analytical technique to be applied.

(ii) X-ray Fluorescence

By far the greater portion of the analytical load is carried by the Philips 1210 instrument. Both solution and pellet techniques are employed, the X-ray tube being a gold target.

(a) Solutions

W and Mo are determined in solutions of sodium tungstate and molybdenum tungstate over the concentration ranges 0-10g/litre and 200-350g/litre, also trace As in the same solutions over the range 0.1-0.2g/litre. Nb and Ta (30-70%Nb, 0.1-5%Ta) are determined in solutions of Fe-Nb.

(b) Pellets

The pellet technique involves the grinding of all component materials down to < 400 mesh. The pellet mixture (10g sample + 3g Whatmans CC31 cellulose binder) is pressed in a 1 1/16" dia. die at 40 tons pressure, producing an exceedingly hard and strong pellet.

The following analyses are carried out on a routine basis: Sn over the range 0,05-0.50% in columbite; Ca, As and Sn in wolfram ore in amounts < 0.5%; Al (35-40%) and C, Si and Mn up to 1% in ferro-aluminum; Cu, Fe, Mn, Cr, V, Si, Al and Ti (40-70%) in ferro-titanium.

For the analysis of niobium ores (Araxa pyrochlore), a modified pellet technique is used, employing Cu as internal standard. Again, all materials are first ground to <400 mesh. Pellet composition: 0.25g sample, 10g CuO, 3g cellulose binder, pressed at 40 tons.

This technique is utilised for the determination of:

Si over the range 0.5 - 2.0,

Nb_2O_5 over the range 50-60%.

Mr. L. Giles stressed that, from their experience, the success or otherwise of their pellet technique was dependent almost entirely upon careful control of sample preparation. In every case the sample (as received in bulk form), cellulose binder, and copper powder were ground to <400 mesh by their own sample preparation equipment - a German (Sieb-Technik) rotary disc mill with tungsten-carbide inserts.

(h) Iron and Steel

The iron and steel industry in the U.K. as a whole employs emission vacuum direct-reading spectrometers on a large scale. At the moment, however, there exist only two instances where these instruments are connected directly to a computer. As yet, the perfection of a closed loop system for completely automated production of iron and steel has still to be accomplished, although development work is proceeding slowly with that end in view.

13. Steel, Peech and Tozer, Ltd. (branch of the United Steel Companies Ltd.), Rotherham

In 1939 the writer was responsible for the installation at S.P. and T of the Hilger large quartz spectrograph. Until his transfer to the Research and Development Dept. of United Steel Cos. in 1948, he supervised its progressive development and application to the routine analysis of plain-carbon and low-alloy steels and associated materials. In 1953, working in an advisory capacity from United Steel Cos.' R and D, he contributed largely to the ultimate installation at S.P.T. (in March 1954) of the first A.R.L. "Quantometer" to be applied within the U.K. steel industry. During the intervening years, due mainly to the enthusiasm of the present Chief Chemist, Mr. P. Dunhill, and his Chief Spectrographer, Mr. W. Sykes, the instrumentation has been gradually augmented to its present formidable capacity.

A. Equipment

3 A.R.L. "Quantovac" spectrometers
1 " "Quantometer"
1 Hilger large quartz outfit
1 English Electric KDN2 computer (8K capacity)

B. Applications

(i) Vacuum Emission Direct-Readers

The three Quantovacs have identical programmes fitted to the analysis of plain-carbon and low-alloy steels. All three instruments are coupled directly to the computer, so that any two can be used simultaneously. The integration banks of these spectrometers have been greatly modified to permit the direct transmission of each element signal to the input-output console of the computer via the computer's own amplifier and by-passing the amplifier normally employed in each spectrometer.

Periodic checks of the analytical programme of each "Quantovac" are carried out by sparking the "High" and "Low" standards, whereupon the computer programme will automatically correct for any drift which may have occurred. However, to ensure that this re-adjustment has been correctly applied it is necessary then to spark a third (intermediate) standard.

Normal analytical procedure is to spark the two halves of a sample simultaneously on any two of the three "Quantovacs". Charges on all integrations are monitored by the computer and the individual results for each half-sample printed out via one teleprinter - if the duplicate results fall within previously agreed acceptable limits, they are printed in black; if unacceptable, printed in red. If acceptable, the computer simultaneously prints out the mean results by a second teleprinter on to a pro-forma laboratory analysis card, works out the finishing additions to be made to that particular cast of steel, and feeds the entire information to a remote Ferranti Argus 100 computer installed in the Central Offices controlling electric-arc furnace operations.

If the initial duplicate results are unacceptable, the mean results are not transmitted to the Argus 100 and the KDN2 signals the procedure to be carried out, e.g. re-spark, or reject sample.

Development work is proceeding to give full automatic programming of the six electric-arc furnaces, including power requirements.

(ii) Sampling Techniques Used in Conjunction With Direct-Reading Analysis

Two methods of sampling are employed:

(a) The orthodox cast cylinder, 1 1/2" dia. x 3", cut into halves and the cut faces prepared by linishing*.

(b) Pin sampling by suction technique, from killed steel in the sampling spoon. The sampling tube is of Pyrex glass, 3.5-mm precision bore, 225 cm. long; the suction applied manually via a rubber bulb at one end of the tube. The temperature range for sampling should not be greater than 1650°C, nor less than 1560°C.

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*Surface grinding on a rotating aluminous-grit paper disc.

Typical Excitation Source Settings for Pin Sample Analysis:

	C(mfd)	R(ohms)	L(micro-henries)
A. R. L.	5	5	360
Jarrell-Ash	30	1.5	50
Steel, Peech and Tozer	25	1.8	50
Stewarts and Lloyds	10	3	50

(iii) Quantometer

Although superseded by the "Quantovacs", this instrument is still busily employed with the analysis of steel scraps and miscellaneous steel samples where the determination of C, S and P is not required. It is also applied, in conjunction with a rotating disc electrode, to the solution analysis of steel-making slags.

(iv) Large Quartz Spectrograph

This equipment is still usefully employed with the odd qualitative or semi-quantitative examination of materials which by nature of their physical form and composition (e.g. corrosion residues, ferro-alloys) cannot be analysed by the direct-readers.

14. Lysaght's Normanby Park Steelworks, Scunthorpe

This plant possesses only the second example of computer treatment of vacuum emission direct-reading spectrometers in U.K. Here a different approach has been made from that at Steel, Peech and Tozer. In the latter instance it is the computer which makes the decision to transmit the analytical results; at Normanby Park, although the read-outs from the "Quantovacs" are monitored by the computer, it is the operator who makes the decision as to whether they are acceptable or otherwise. In effect it would appear that the computer is not being utilised to its full advantage, but it should be pointed out that the requirements of the 2-slag refining process in L. D.* steel-making are somewhat different from those of electric steel-making at S. P. and T.

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*Linz-Donowitz basic oxygen process.

A further significant difference in practice with the Lysaght's computer is that it is not coupled directly to the integrators of each of the 3 spectrometers but accepts the individual readings sequentially via the amplifier of each instrument.

A. Equipment

1 standard A.R.L. "Quantovac" programmed for iron and steel
1 wide-range " " " " iron, steel and slags
1 A.R.L. "Uvaq" air/vacuum spectrometer programmed for iron, steel and slags
1 English Electric KDN2 computer (8K capacity), housed remotely from the Laboratory and closely adjacent to the L.D. converter

B. Applications

In the original concept of a computerized system it was intended that the "Quantovac" Laboratory would provide the ultra-rapid analysis of blast furnace and mixer irons, L.D. slags, and production bath samples, from all of which the computer would calculate the heat balance, oxygen required and charge additions for each cast. So far, after some 2-3 years, this operation has not proved entirely possible.

Present analytical practice produces, via the computer, duplicate analyses of the sample via any two of the three instruments. The final mean analysis, after vetting by the operator, is transmitted back to the computer for incorporation in the charge-addition programme.

The analysis of blast furnace and L.D. slags is carried out by means of a fusion/graphite pellet technique with added internal standard, the calibrations, as with those of metal analysis, being stored in the computer memory. Such slag analyses are put through on a post mortem basis, however.

The pellet composition consists of 0.5g sample, 2.5g buffer (prefused 60% lithium tetraborate, 30% strontium tetraborate, 10% cobaltic oxide). The mixture is fused in a graphite crucible for 5 minutes at 1050°C and the resultant melt poured into a water-cooled stainless steel block. The glass bead, together with 2.5g graphite powder (Grade 2), is ground in a vibratory disc mill for 25 seconds, followed by pressing the resultant powder under 30 tons pressure in a 15/16"-internal-diameter hardened steel die.

Work is now proceeding to accumulate sufficient data from which to write a computer programme capable of co-ordinating an integrated system for full automatic control of L.D. steelmaking. However, the problem at Normanby Park works, by reason of the rather complex nature of the

2-slag L.D. process, is significantly more formidable than with the electric-arc process at Steel, Peech and Tozer.

15. G.K.N. Group Research Laboratories, Wolverhampton

The Guest, Keen and Nettlefold Group controls a number of iron and steel plants, of which Lysaght's at Scunthorpe comprises one unit. The Research Laboratories at Wolverhampton are responsible for all research and development work within this group of companies and to a great degree dictate the technical policy throughout the group. The Chief Research Chemist, Mr. G. Croall, has been largely responsible for developments in the field of chemistry and physical chemistry. The emission direct-reading spectrometers now in routine operation at the 3 main G.K.N. plants were installed according to specific recommendations.

A. Equipment

(i) Emission

1 Hilger large quartz outfit
1 A.R.L. wide-range "Quantovac", equipped with additional (air-path) excitation stand carrying a Danielsson tape machine for the analysis of oxide-type materials

(ii) X-ray fluorescence

1 Philips 1540 vacuum X-ray fluorescence spectrometer and ancillary electronics

B. Applications

(i) Emission

Initially obtained in order to explore its possible applications within the G.K.N. Group, as well as supply an analytical service to the Research Laboratories, the large quartz spectrograph is now used only for occasional semi-quantitative and quantitative analyses as required.

The A.R.L. wide-range "Quantovac" was obtained for a two-fold purpose:

(a) to determine the possible role of the "Quantovac" in iron and steel production at G.K.N. plants;

(b) to investigate the application of the tape machine to a wide range of slags, iron ores, refractories and other oxide-type materials.

Arising from the foregoing investigations, the main G.K.N. iron and steel plants are now equipped with A.R.L. "Quantovacs" with analytical programmes chosen for the particular requirements of each plant. The present chief application of the wide-range "Quantovac" at Wolverhampton is to current B.I.S.R.A. spectro-chemical investigations.

(ii) X-ray Fluorescence

Like the "Quantovac", the Philips PW1540 was acquired to investigate its capabilities with respect to the analysis of a wide range of iron and steel-making materials. G.K.N.'s contributions in this field, particularly in collaborative work within B.I.S.R.A., have been of value in highlighting significant differences between identical X.R.F. instruments installed throughout U.K. At the time of this visit, work was proceeding with the analysis of iron ore sinter.

As yet, no decision has been made regarding the possible installation of X.R.F. equipment at any of the G.K.N. plants.

16. S. Fox and Co. (branch of United Steel Cos.), Stocksbridge

This particular branch of U.S.C. specialises mainly in the production of austenitic and ferritic stainless steels (brand name "Silver Fox") and, to a lesser extent, plain-carbon and low-alloy steels. The analytical services for the Electric Arc Plant are housed in one Central Laboratory in the charge of Chief Chemist Mr. R.F. Statham.

A. Equipment

1 A.R.L. "Quantometer"
2 "Quantovacs", one equipped with teleprinter read-out
1 Hilger large quartz outfit

B. Applications

The Hilger large quartz outfit is now rarely used and then only for ad hoc investigations to which direct-readers cannot be applied.

The 2 "Quantovacs" provide a 24-hour, 3-shift coverage for steel production control requirements, for all steels except maraging qualities, which are generally analysed chemically. The A.R.L."Quantometer", installed in 1956, is still used for the analysis of stainless pit samples for the major alloying constituents and residual impurities.

As yet, no great consideration has been given to the possibility of a computer hook-up to that at Steel, Peech and Tozer, but in view of the close liaison maintained between the various U.S.C. branches there is little doubt that this system will eventually materialise.

Sampling

For "Quantometer" and "Quantovac" operation, the orthodox cast cylinders are employed. However, because experience has shown that the cooling rates of such samples are extremely critical with respect to analysis, these samples are transported from the Plant to the Laboratory while still hot from the mould. Transportation is by high-speed Lamson pneumatic tube system, utilising special heat-proofed containers. On arrival each sample is cut hot by means of a high-speed abrasive wheel and then water-cooled under controlled conditions prior to analysis. By these means the incidence of cracked samples is kept remarkably low.

Pin sampling is also carried out as at S.P. and T, but using evacuated Pyrex tubes.

The Company has now decided that, so far as finished materials are concerned, analysis by X-ray fluorescence would be simpler and for this purpose a suitable automatic X.R.F. spectrometer will be installed in the near future.

17. United Steel Cos.' Research and Development Dept. (Swinden Laboratories), Rotherham

The extensive applications of instrumental analysis throughout the Company's various plants have been largely guided by thinking and exploratory investigation from the Analytical Chemistry Section, now headed by Mr. G. Padget. In the early days the policy was to advocate the installation of recommended emission direct-reading equipment in the actual plants rather than in the Research Laboratories. A notable exception was the installation of the A.R.L. Slag "Quantometer", the development of which became the responsibility of this writer (G.L.M.) in July 1959.

The increasingly rapid development of the X-ray fluorescence technique in the late '50s and early '60s, coupled with the availability of two extremely capable X-ray physicists (Dr. H. Hughes and Mr. W. Johnson) within the Dept., led to an extensive exploration into the possibilities of this technique. It is now reasonable to predict that suitable X.R.F. equipment will shortly be installed at the 3 main U.S.C. steelmaking plants.

A. Equipment

(i) Emission

1 Hilger large quartz outfit
1 A. R. L. "Standard Slag Quantometer"
with digital print-out

(ii) X-ray Fluorescence

1 Philips PW1540 vacuum X. R. F. spectrometer
1 " "Autrometer"

(iii) Atomic Absorption

1 Hilger atomic absorption spectrometer

B. Applications

(i) Emission

The considerable amount of steel analysis previously carried out with the large quartz instrument has now been transferred to the "Autrometer". The large quartz is now used only for the odd unknown residues and metals, also in conjunction with the micro-spark traverse attachment for the identification and analysis of segregates and inclusions in steels.

The "Slag Quantometer" is still used extensively for the analysis of iron ores, slags, and refractories by means of the "Rotrode" solution technique.

(ii) X-ray Fluorescence

The "Autrometer" is extensively employed in the analysis of a large number of experimental plain-carbon and low-alloy steels with which chemical analysis simply could not cope.

The PW1540 is applied mainly to the solutions analysis of stainless and high-alloy (maraging) steels. On a less extensive scale it is used for the analysis of inclusion residues and also for the analysis of slags.

Work is proceeding on the calculation of the correction factors for the several interferences normally experienced when analysing solid samples. When this is accomplished, a computer link-up will be provided to permit the rapid interpretation of data into results and so eliminate the need to use the more time-consuming solution technique.

Sample Preparation

For all the X.R.F. analyses of steels at Swinden Labs., the sample is prepared by means of a "Lap-Master" machine which laps (or grinds) the surface with a boron-nitride paste. By this means, 12 samples can be prepared simultaneously in 30 minutes, the face of each sample being covered with a random distribution of fine, needle-like scratches. It is claimed that this method of surface preparation effects a significant improvement in counting reproducibility.

(iii) Atomic Absorption

The recently installed Hilger A.A. spectrometer had been little used, but the determination of small amounts of lead was undergoing investigation.

18. Firth-Brown Ltd. and Brown-Firth Research Laboratories, Sheffield

The Central Laboratory, serving the Siemens and electric arc furnaces, and the Analytical Research Chemistry Section in the Research Laboratories are both under the control of the Laboratory Manager and Chief Research Chemist, Mr. B. Bagshawe.

Central Laboratory

A. Equipment

Emission

1 A.R.L. "Quantometer"
2 " "Quantovacs" with digital print-out

B. Applications

The "Quantovacs" are continously employed on the production control analysis required by both the Siemens and electric arc plants, which between them produce a wide range of plain-carbon, low- and high-alloy steels. For high-alloy analysis the ratio technique of calibration is employed, together with empirical corrections determined by the performance of a previously run standard which can be any one of 600, according to the specification of the analysis sample. Maraging steels are analysed as routine by the same practice.

In view of the extensive calculations at present carried out by a Monroe calculating machine, the Operations Research Dept. has purchased an American computer, the "PDP-8" (8K capacity), made by Digital Equipment Corporation, U.S.A., and a computer programme now undergoing preparation will eventually replace the Monroe with a corresponding significant saving in analysis time (at least 10 minutes per sample).

The A.R.L. "Quantometer" is used mainly for the analysis of miscellaneous steels when the determination of carbon, sulphur and phosphorus is not required.

Brown-Firth Research Laboratories

At the time of the visit, these laboratories had recently been re-housed in a modern 5-storey block involving an overall cost of $2.25M. Although a well-equipped Research Chemistry Laboratory provides the analytical services so essential to such an organisation, the overall analysis is applied on a small scale only. As yet, the acquisition of X-ray fluorescence and atomic absorption equipment has still to be considered.

A. Equipment

2 Hilger large quartz outfits
1 " medium " outfit

B. Applications

(a) Quantitative and semi-quantitative identification of miscellaneous plain-carbon, low- and high-alloy steels.

(b) Analysis of steel-making slags (electric arc and Siemens) by the Rotrode solution technique.

(c) Qualitative and semi-quantitative analysis of residues.

19. Hadfields Ltd., East Hecla Works, Sheffield

At the time of this visit the Company was undergoing a major re-organisation and the visit was confined to the Spectrographic Laboratory headed by the Chief Chemist, Dr. J. Hobson. This laboratory provides the essential routine production control analysis for the Steel-making and Foundry departments.

A. Equipment

1 Hilger large quartz outfit
1 Hilger "Polyvac" E600 vacuum emission spectrometer equipped with the original Hilger low-alloy computer, now extensively modified to provide high-alloy analysis.

B. Applications

The "Polyvac" provides all the analyses required for production control for steel-making and foundry work. The analytical programme of the instrument is of a wide nature covering plain carbon, low- and high-alloy steels (but not the maraging steels, which are analysed chemically).

The circuitry of the low-alloy computer has been drastically modified by the Electronics Engineer in order to cope with a wide analytical range of high-alloy steels, and now provides for a total of 15 known interference corrections. Although its circuitry is more complex than the new Hilger high-alloy computer's, in operation it is at least equal to, if not better than, that instrument. Calibrations for the high-alloy ranges are based on the now universally applied Ratio Technique.

20. Stewarts and Lloyds Ltd., Dept. of Research and Technical Development, Corby, Northants.

Without doubt no other research organisation within the U.K.'s iron and steel industry has contributed more to the furtherance of spectrochemical methods of analysis during the past two decades. Throughout this period, Mr. S. Muir, now Superintending Research Chemist, has been closely associated with the progressive development and application of both emission and X-ray fluorescence techniques.

The visit to Corby covered both the D.R.T.D. Spectrographic Laboratory and the Works Spectrographic Laboratory.

I. D.R.T.D.

A. Equipment

1 Hilger large quartz/glass outfit
1 Hilger "Fluoroprint" X.R.F. spectrometer

B. Applications

The large quartz/glass outfit is now used largely for the analysis of inclusions extracted from steel, the "Rotrode" solution technique being employed. Odd miscellaneous steels are also analysed by the argon-spark technique.

The "Fluoroprint" is used for the analysis of low-alloy and stainless steels (solid-sample technique), previously using close group calibrations but now moving over to a universal calibration in conjunction with data processing incorporating a computer. The instrument is also used for the analysis of slags and refractories in conjunction with a "glass" disc technique - the sample is fused with a sodium tetraborate (1:9) with the addition of lanthanum oxide as buffer (twice the sample weight). The "glass" disc is obtained by casting the fusion in a graphite crucible.

II. Works Laboratory

A. Equipment

(i) Emission

1 A.R.L. "Quantometer" (installed in 1954)
3 " "Quantovacs" (the first installed in 1957, the last only recently)

(ii) X-ray Fluorescence

1 A.R.L. VXQ automatic X.R.F. spectrometer (fixed channels)
1 Hilger "Fluoroprint" X.R.F. spectrometer

B. Applications

(i) Emission

The A.R.L. "Quantometer", first used as a trial horse for the direct-reading analysis of iron, steels and slags, is now used only for the analysis of blast-furnace and mixer iron.

The "Quantovacs" provide all the routine analyses for the production control of L. D., electric arc and basic open-hearth steel-making. For the analysis of stainless steels the Ratio method is applied. Work has also been carried out, as at S. P. and T., investigating the possibilities of utilising cast pins as sample electrodes; so far the results with this technique have been rather variable.

In conjunction with D. R. T. D., an exploratory investigation has been carried out looking into the possibilities of combining the pin-sample technique with the installation of a "Quantopact" (small, packaged edition of the "Quantovac", 12 elements only) on the melting stage of S. and L's Bilston works. Completion of this project has shown that little or no advantage is to be gained over the orthodox system.

(ii) X-ray Fluorescence

The A. R. L. VXQ instrument was obtained specifically for the rapid routine analysis of iron-making slags and iron ore sinters and from the outset has been a pronounced success. Sample presentation is by means of the lead-ring technique, no binder being required.

The more recently acquired Hilger "Fluoroprint" was purchased for its flexibility as compared with the inflexible analytical programme provided by the VXQ. The instrument is applied mainly to the analysis of stainless steels (solid-sample technique), but has also been applied successfully to the analysis of slags and sinters and, as such, is used as a stand-by for the VXQ.

(As an analytical tool, the operators prefer the "Fluoroprint" to the VXQ.)

SUMMARY AND CONCLUSIONS

Most probably the greatest sustained development of spectroscopic analytical techniques in the U.K. during the past decade has taken place within the field of emission spectroscopy. This is particularly evident when one considers the now widespread application of the emission direct-reading spectrometer throughout the metal industries. The limited inflexible analytical programmes of such instruments have inevitably confined their application more or less to routine operation, the majority of such applications (now well over 100) taking place within the iron and steel industry. Here, the use of the modern vacuum emission D. R. spectrometer has become so indispensable to the control of rapid steel production that it is now standard practice in all the major plants within the U.K. and in many of the smaller plants. The present trend of development with this type of instrument now concerns its introduction into the non-ferrous metals industry and particularly to copper-base and aluminum-base alloys. Present indications are that, notwithstanding the undoubted quality of available instruments, a considerable amount of analytical development is necessary before their successful application is to be achieved.

The application of the X-ray fluorescence spectrographic technique in the U.K. has progressed by no means so rapidly as with the optical emission. Its application to the lighter elements below atomic number 22 has, until fairly recent developments, proved most disappointing. However, there is no doubt that, within the metals industry at least, too much was expected of the technique at a time when there existed a sad lack of appreciation of the physical limitations and the fundamental knowledge of how to overcome or correct them. It is not surprising, therefore, that the technique has undergone severe criticism and has been considered with the greatest suspicion. More extensive developments of recent years, coupled with the production of more efficient counters, new analysing crystals and, more recently still, computer data-processing to cope with the often complex fundamental calculations, have given rise to a greater appreciation of its undoubted potentialities. As a research tool, by reason of its greater flexibility, the X-ray fluorescence spectrograph holds a distinct advantage over its emission counterpart and it is in the field of research in the U.K. that, so far, it has found its greatest application. Nevertheless, there already exist a number of routine applications within industry (both ferrous and non-ferrous) involving the use of fixed channel automatic X.R.F. spectrometers, and it is interesting to note that in this respect Philips will shortly be introducing a 7-channel automatic instrument.

Of the three analytical techniques under consideration, atomic absorption is by far the youngest, its potentialities first being expounded by Walsh as recently as early 1955. However, like its fellow its early application development suffered somewhat from the lack of suitable instrumentation, and it was not until 1960 that any real progress was made. During the past 3 years the production of more precise and sophisticated equipment has resulted in a surge of development work throughout the U.K., where the technique is being employed on an ever-widening basis, both in research and routine operation. Where previously by reason of its great sensitivity the technique was first thought of in terms of trace analysis, its application is gradually being extended to the determination of major constituents.

An attempt has been made to survey, so far as was possible, the current applications of spectroscopic methods of analysis (emission, X-ray fluorescence, and atomic absorption) throughout industry and research in the U.K. Arising from this survey it is obvious that rapidly increasing use is being made of such techniques (preferably on a direct-reading basis) over a wide field, to the extent that they are being applied wherever possible to the exclusion of tedious and time-consuming chemical procedures. This is particularly evident within the non-ferrous and ferrous metals fields.

Despite their respective advantages, it is nevertheless clear that none of the three techniques can claim overall superiority; rather is each supplementary to the other two.

G. L. Mason,
Senior Scientific Officer.

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APPENDIX I. - Itinerary, July 3 to August 1, 1967

DATE 1967	ESTABLISHMENT VISITED
July 3	International Nickel Research Laboratories (Mr. K. Bills), Edgbaston, Birmingham.
4	Imperial Metal Industries (Kynoch) Ltd. (Mr. W. T. Elwell), Witton, Birmingham.
5	G. K. N. Group Research Laboratories (Mr. G. Croall), Lanesfield, Wolverhampton.
6, 7	Summer Conference of the Spectroscopy Group, Institute of Physics and The Physical Society.
10	Imperial Smelting Corporation Ltd. (Mr. Cosham), Avonmouth.
11	U. K. Atomic Energy Research Establishment (Mr. M. Webb), Harwell.
12	Mullard Radio Valve Co. Ltd. (Mr. C. R. Gentry), Mitcham, Nr. London.
13	Johnson, Matthey and Co. (Mr. D. J. Hobbs), Wembley, London.
14	Stewarts and Lloyds Ltd.,, Dept. of Research and Technical Development, Corby, Northants. (Mr. S. Muir).
18	D. S. I. R. Warren Springs Laboratories (Dr. P. G. Jeffery), Stevenage, Herts.
19	Henry Wiggin and Co. Ltd. (Mr. D. Jukes), Hereford.
20	London-Scandinavian Metallurgical Co. Ltd. (Mr. G. Holmes), Templeboro, Rotherham.
21	Hadfields Ltd. (Dr. J. Hobson), East Hecla Works, Sheffield.
24	Lysaght's Ltd. Normanby Park Works (Mr. A. K. Wright), Scunthorpe, Lincs.

July 25	Yorkshire Imperial Metals Ltd. (Mr. J. Cross), Leeds.
26	a.m.: Steel, Peech and Tozer Ltd., (Mr. W.S. Sykes), Rotherham.
26	p.m.: United Steel Companies Ltd., Swinden Laboratories (Mr. G. Padget), Rotherham.
27	Firth-Brown Ltd., and Brown-Firth Research Laboratories (Mr. B. Bagshawe), Sheffield.
28	S. Fox and Co. (Mr. R.F. Statham), Stocksbridge, Nr. Rotherham.
31	B.N.F.M.R.A. Laboratories (Dr. Reynolds), Euston Street, London.
Aug. 1st	Mullard Research Laboratories (Mr. E. Millett), Salfords, Nr. Redhill, Surrey.

APPENDIX II

The Institute of Physics and The Physical Society

Spectroscopy Group

Summer Conference

on

Accuracy of Spectroscopic Methods,

University of Birmingham, 6-7 July 1967

The programme consisted of 8 invited and 8 contributed papers, as given in the attached list. A total of approx. 140 delegates were in attendance, comprising 18% from instrument manufacturers, 31% from research organisations, 10% from academic professions, 10% from government laboratories, and 31% from industry.

The proceedings of the conference will not be circulated or published.

Impressions

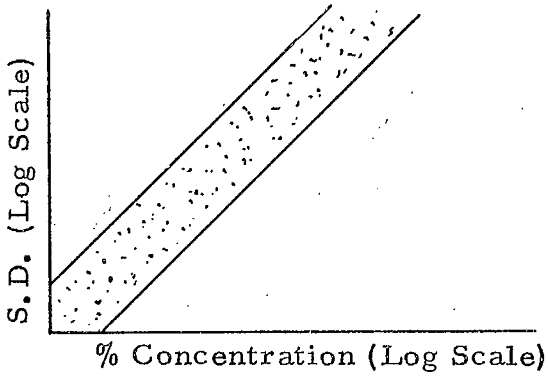
Of the very mixed bag of 16 papers, only one-half could be said to conform truly with the actual theme of the conference. The authors of the remaining papers, including some of the invited ones, used the theme merely as a platform from which to mount their favourite hobby horse.

Nevertheless, the Conference got off to a good start, the opening paper by C. E. A. Shanahan arousing considerable and at times heated discussion, which was resumed later during the Speakers Forum. The remaining notable papers were presented by M. D. Amos, W. Ramsden, R. Jenkins, D. Sumter, Dr. K. J. Ross, W. E. Clarke, and D. J. Hobbs.

It is interesting to note that Shanahan's paper drew forth a remarkable illustration by E. H. Oswin (United Steel Cos.' Research and Development Dept.), which was presented during the Speakers Forum. In common with Shanahan, Oswin met with some opposition, yet it seemed that the dissentients had completely missed the significance of the point he was making.

Oswin was reporting on some observations made at U. S. C. Research Labs. in connection with recorded referee analyses of a large number of B. C. S. standard samples (irons, steels, slags, refractories, iron ores, sinters, etc.) carried out by the various collaborating analytical laboratories.

From the data available a log/log plot had been made, concentration of element or constituent V standard deviation of the analytical results from which that concentration was determined, with the following results:



From the many results involved in the above plot, it was possible to determine the best and the worst precisions in relation to concentration:

Degree of Precision	Metals (Iron and Steels)	Oxide-type Materials (Powders)	
	B.I.S.R.A. chem. anal.	B.C.R.A. chem. anal.	B.I.S.R.A. spectro. anal.
Best	$0.01\sqrt{\text{Concentration}}$	$0.05\sqrt{\text{Concentration}}$	$0.06\sqrt{\text{Conc.}}$
Worst	$0.04\sqrt{\quad}$ "	$0.4\sqrt{\quad}$ "	$0.21\sqrt{\quad}$ "

The above table provides a firm indication of the precision to be expected from referee chemical methods in connection with ferrous and associated materials. The sting is in the tail: with respect to the oxide-type materials, the worst precision to be expected from spectro-chemical analysis should be significantly better than the worst of chemical analysis, and the best almost equal to that of the best chemical analysis.

G. L. Mason

Papers Presented during the Conference

1. "The accuracy and precision of analytical procedures", C. E. A. Shanahan (Richard Thomas and Baldwins Ltd.).
2. "The instrument manufacturer's problem", Mr. R. A. C. Isbell (Hilger and Watts Ltd.).
3. "Factors affecting precision and accuracy in analysis by atomic absorption spectroscopy", M. D. Amos (Techtron Ltd.).
4. "Reduction of excitation and instrument errors in emission spectroscopy", W. Ramsden (Applied Research Laboratories Ltd.).
5. "Influence of the primary X-ray source on analytical accuracy", J. G. M. Fox (Hilger and Watts Ltd.).
6. "Detection of X-rays and data handling systems", R. Jenkins (Philips, Eindhoven, Holland).
7. "Factors affecting accuracy in spectroscopic calibration", D. Swingler (Stewarts and Lloyds, Corby).
8. "The theoretical evaluation of X-ray fluorescence intensities", D. Sumter (Stewarts and Lloyds Ltd., Corby).
9. "An accurate method for the analysis of high alloy steels using a direct-reading spectrometer and an analogue computer", J. B. Baird (Hilger and Watts Ltd., London).
10. "High resolution electron spectrometer study of atomic and molecular collision cross sections", K. J. Ross (Southampton University).
11. "Atomic absorption methods for silicate rock analysis", R. J. Thompson (Imperial College).
12. "Atomic absorption spectroscopy in iron-foundry control analysis", W. E. Clarke (Brit. Cast Iron Research Association).
13. "Progress in emission spectrographic analysis of precious metals", J. H. Bond (International Nickel Ltd.).
14. "A digital readout for improving the accuracy of measurement of spectral-line intensities", D. A. Barrow and J. R. Tilsley (Brit. Steel Castings Research Association).
15. "The errors of D. C. arc excitation in trace analysis by emission spectrography", D. J. Hobbs and B. J. Rees (Johnson, Matthey and Co.).

16. "Present and future state of spectroscopic analytical methods", N. W. H. Addink (Philips, Eindhoven, Holland).

The final session on the last afternoon consisted of a Speakers Forum in which some of the speakers led an open discussion.

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