The Changing Aspect of Chemical Analysis*

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AFTER the visit to the analytical laboratories in the Research Department at the Billingham Division of Imperial Chemical Industries Ltd. earlier to-day, it seems to me that a general type of lecture will be more appropriate than the discussion of a particular topic. I therefore propose to review some of the present tendencies in analytical chemistry, because it is a useful exercise to consider the broad field, rather than the individual plants. This will not enable us to forecast what is going to happen next (if I had given this lecture 8 years ago I could not have mentioned gas chromatography, as it was in 1952 that it burst upon an astonished world), but it may help us to decide which of the plants are most worth cultivating. I am going to talk from the point of view of an industrial analyst, most of whose time is nowadays given to administration, and I propose to rely very largely on my own experience, rather than to make an attempt to review everything. This will leave some gaps, but ought to ensure that the picture is fairly realistic.

I would like to emphasise that I am going to talk about *chemical analysis* and not *analytical chemistry*. The difference is not always sufficiently appreciated, particularly in academic circles, where they teach *analytical chemistry*, and often restrict it to *inorganic* chemistry, not having yet caught up to the fact that organic analytical chemistry is—in industry, in agriculture and, I expect, in public analysts' laboratories—equally important. But in carrying out chemical analysis nowadays we are half the time not primarily concerned with chemistry, but with physics. My Company produced a book on analytical techniques, which has had a certain amount of success. We called it "Analytical Chemistry —The Working Tools," because it was about the tools of the trade. But one reviewer rather acidly pointed out that this title was a misnomer, as there was hardly any chemistry in it, it was mostly about physics. Nevertheless, we are not analytical physicists, but analytical chemists, because what we are interested in is not usually the physical state of our samples, but the chemical composition, and we use any criterion—chemical, physical or biological— that will help us to obtain the desired information. This leads me to attempt a definition of chemical analysis. "Chemical analysis is a body of techniques, chemical and physical, that are used to determine the composition of any substance," and what I am going to talk about this evening is the changes that are taking place in these techniques. I am going to talk about chemistry first, and then physics, though it is very doubtful where one ends and the other begins.

But before discussing details, I want to make two very important general points— chemical analysis is largely empirical in outlook and pragmatical in philosophy, so that theory usually lags behind practice; and it is a purely economic activity, nobody does it for fun or in the pursuit of pure knowledge. In Universities people study, for example, complex poly-acids, because they are intrinsically interesting—to the people who study them. These may go on and show that some of the polyacids have properties that permit them to be used in analysis—that is analytical chemistry. But chemical analysis is practical and, concerned with economics, only studies polyacids in so far as they will make for quicker—and that means cheaper—or more accurate analyses. I expect I shall return to these points again, but whether I do so or not they are implicit in anything that I shall say. To an industrialist, chemical analysis is not—or ought not to be—an overhead, it is part of the cost of production and so is in the same category as plant maintenance. It is something you do to keep up and increase output while ensuring that the product is of the proper quality; even the activities of the public analysts and consultants are ultimately of this kind, and it is the duty of the head of the laboratory to see that his service is efficient and economical. In considering how he is to do this he arrives at two conclusions. (1) What he is producing is information, and every piece of information he supplies has a cash value; and somebody has to decide what his information is really worth. (2) That the most expensive ingredient in almost every analytical report is *laboratory time*. As he probably can do little about item (1) (it is the customer, not the supplier, who ultimately decides how much any product is worth), he

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wisely devotes himself to (2), and asks himself "How can I supply analytical information quicker than I do now, without loss of necessary accuracy?" There are actually two ways he can approach this problem; the first we are not concerned with tonight. It is to ask the question "Are all these analyses really useful?" and to arrive at the answer he will have recourse to statistical analysis in some form. The second approach is to look for new methods of analysis, and ultimately this is the driving force behind most of the research in analytical methods now going on. I know that some new methods are devised to be more accurate than old ones, and this is particularly so in organic analysis, but even then that accuracy has an economic value—and, moreover, most of the new organic methods are relatively rapid. But, generally, improved accuracy is not the chief point; either information is wanted on new subjects or information on old subjects is wanted quicker. How the information is being obtained will be the subject of the rest of this talk, and I propose to divide it into two parts, (1) largely chemical and (2) largely physical.

In the chemical field, I want to look at the progress being made in several lines. They are—

A. Micro analysis.

B. New reagents, including the non-specific chelating reagents.

C. Use of non-aqueous solvents.

D. Electrochemistry.

It is arbitrary to divide up the subject in this way; an actual analysis may spread over two or three categories, but for convenience we can use this classification.

Micro analysis of course is not new, but its use is increasing. It is not only as accurate —when applied to organic analysis—as macro analysis; it is quicker. It needs a manipulator with a very nice pair of hands, who need not be a very skilled chemist—in fact need not be a chemist at all. I remember during the second World War we had a girl who could complete 8 or even 10 micro Dumas nitrogen determinations per day, on quite awkward samples, but whose knowledge of chemistry was rudimentary. On the other hand, not everybody has the right temperament—apart from manual dexterity—to make a micro analyst. It is true that the endeavours of Belcher and others have much simplified the technique, and that there are automatic furnaces—at a price—that are very satisfactory, and much of that aura of sanctity that used to surround micro analysis is disappearing. Still, it is an exacting technique, and I am not sure whether a change to semi-micro analysis is much of an improvement. Advances are, however, always being made. Mettler-type balances make weighing simpler, for a start; the use of analysis by functional groups instead of for elements is increasing; the Schöniger method of combustion in oxygen enormously simplifies the determination of halogens and sulphur, and when we have combusted our sample and caught the products of combustion there are all kinds of clever ways we can use to complete the determination, and we ought to consider what justification we have for continuing to use some of the older methods. For example, every time I see somebody carrying out a gravimetric sulphate determination by barium sulphate, either on the micro or on the macro scale, I ask myself how much progress has really been made since Berzelius said that Swedish filter-papers (as "used by all the most clever chemists") were the best in the world.

We all know that the gravimetric method is tedious, we all ought to know that it is largely empirical, and only gives the right answer by compensation of errors. I grant that it is reproducible, but that is only half the story. Recently several quicker ways have been described. Archer[1] dilutes his aqueous solution with acetone, adds a little dithizone, which is soluble in acetone, and titrates with $0.01 N$ lead nitrate of which 1 ml is equivalent to 0.15 mg of sulphur in solution. As long as there is any sulphate, the lead is precipitated; as soon as there is a minute excess of lead, the green dithizone turns pink. Of course there have to be no heavy metals present, such as zinc, which can so easily be extracted in traces from some kinds of glassware, but it is very easy to clean up the solution by passing it through a column of base-exchange resin. This method can also be used for larger samples simply by diluting the solution and taking a small aliquot, as we need no longer be frightened by the bogy of introducing errors through successive dilutions. With proper use of calibrated apparatus, the errors introduced by dilution are insignificant compared with other errors in an analysis.

There are two other methods of titrating sulphate that we have found useful, one depending on lead and the other on barium as the reagent. Both are interesting and exemplify the fresh approaches being made to this kind of test. In the first,[2] an ingenious use is made of an oxidation - reduction system to locate the end-point. To the solution containing sulphate one adds a few drops of a very dilute solution containing ferro- and ferricyanide, then alcohol to lower the solubility of the lead sulphate, and titrates with dilute lead nitrate solution. As long as sulphate is present, the ratio of ferro- to ferri- remains constant and the redox potential of the solution measured by a platinum electrode is also constant. When all the sulphate is precipitated, the next drop of lead precipitates lead ferrocyanide, leaving ferricyanide unaffected, and there is a sharp change in the potential of the indicating electrode. This system works very well: we have recently been doing some phase-rule studies that necessitated dozens of determinations of sulphate ion, and all of them were made in this quick and accurate way. Of course the method is not free from interferences, phosphate interferes, calcium interferes, and both these ions can interfere in another useful titrimetric method for sulphate—titration with barium chloride solution with alizarin S as an adsorption indicator.[3] To sum up, there is not as yet a volumetric method for sulphate as free from interferences as the old gravimetric method, but there are several volumetric methods of fairly wide application, and we ought to ask ourselves "Should I be spending time on a gravimetric method for this particular sample, or should I be saving time by using a volumetric method?"
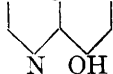
I have wandered rather a long way from micro analysis, but I wish to make the point that in both micro and macro analysis, gravimetric methods ought to become less and less common; this will not result in loss of accuracy and will achieve a vast saving of time. Only too often gravimetric analysis is a kind of sacred cow that wanders about in the laboratory helping itself to samples that it slowly consumes, and gives in return—what? A wholly misplaced trust in the idea that because we can weigh accurately, the analysis is accurate; but how often do we *really* know that the solid we have precipitated is pure and that precipitation is complete? No precipitate is quite insoluble, and almost every precipitate tends to drag down other substances with it; sometimes it is fairly easy to purify the precipitate, but not always. One can almost make a general statement that if possible one should avoid gravimetric determinations.
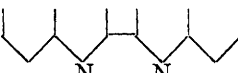
Nowadays there are so many ways of measuring quantities without using the balance that, particularly for small amounts, there is usually some better way of doing it. Volumetric analysis, either with indicators or electrical methods of indicating the end-point, spectrophotometry, polarography, should all be considered before resorting to the tedious business of precipitation, washing, re-dissolving, re-precipitating, washing again, drying, or calcining, cooling and weighing that constitutes gravimetric analysis.

I must pass on to a brief consideration of some of the new reagents. They illustrate rather well the empirical nature of chemical analysis. Anything goes, as long as it leads to the correct answer. Some day somebody will write the fascinating history of analytical reagents, and I believe that it will be shown that most of them were discovered in the first place by accident and that development work of a secondary kind was systematic. I do not think that Tschugaeff was trying to find a reagent for nickel when he discovered the intense crimson compound of nickel with dimethylglyoxime, but the man who first applied it as a highly selective reagent for palladium was surely guided by his knowledge of the periodic table. The first observation that 8-hydroxyquinoline could have analytical uses was certainly accidental. 8-Hydroxyquinoline potassium sulphate was originally used as a disinfectant of the intestinal tract, and in a note in *The Analyst* in 1918[4] it was pointed out that the solution was occasionally turbid and that the turbidity or precipitate was due to *copper*. It was suggested that the drug might have uses as a sensitive reagent for copper, and the next paper (in 1927) was also on copper; its use for aluminium and beryllium was 2 years later. Callan and Henderson, who first applied sodium diethyldithiocarbamate as a colorimetric reagent for copper, did not invent a new reagent, they exploited an observation that the chemical—already in production commercially—turned yellow if the least trace of copper got anywhere near it. Thioglycollates were not invented as colorimetric reagents for iron, and when Schwarzenbach began his classical investigations on ethylenediaminetetra-acetic acid, he did not have the analyst in mind. In 1933, Lundell of the Bureau of Standards in a fascinating paper[5] on the "Analysis of Things As They Are," a paper that ought to be prescribed reading for every analyst, said that in heaven there will be a shelf with 92 reagents

on it, number 13 being specific for aluminium, number 26 the sure shot for iron, number 39 the unfailing remedy for yttrium, and so on, but Lundell knew that this had not arrived yet. And we know now, thanks to the work of Irving and others, that it is not unlikely, it is impossible. True, we can make a selective reagent behave specifically in some cases by the skilful use of masking reagents, and a modern inorganic analyst must devote considerable attention to the equilibria that are involved. It is still in a sense true that any fool can do the determinations if an analyst tells him how to do the separations, but to-day our means of doing the separations are so much more varied than they used to be. I am not sure whether, when all the froth of papers on EDTA has subsided, it will not be found to be almost as useful a masking reagent as it is a titrant; for example, at the right pH, beryllium is the only metal precipitated as a hydroxide in presence of EDTA, and ammonium magnesium phosphate is almost the only phosphate. This leads us to the present-day idea that you separate only what you want to determine, *i.e.*, by precipitation or extraction, and leave all the other constituents behind. That is, separations tend to be more specific and more complete than they used to be.

But even though there is now some measure of system in the devising of organic reagents for metals, there is none in forecasting the occurrence of insolubility in inorganic

compounds. We all know that the group [structure] will combine with almost everything,

that [structure] is specific for copper and that if you put large groups too near the

N steric hindrance will prevent compound formation from taking place, but so far as I am aware, we don't *really* know what confers low solubility in water on one compound and not on another. And from time to time fascinatingly improbable compounds turn up and solve a previously difficult problem. The triple uranyl acetates permitted sodium to be readily determined; $Cd[CS(NH_2)_2]_4Cr(CNS)_5OH.H_2O$ is almost insoluble, whereas the corresponding zinc salt is soluble. Who could have forecast that $[Co(NH_3)_6][(H_2O)_2Be_2(CO_3)_2(OH_3)]$ is readily prepared and is insoluble?[6] It is a compound of an unusual type and it may make a useful contribution to the analytical chemistry of beryllium.

But what we analytical chemists need more than lots of new and better reagents is more courage and skill in dropping some of the old ones. It is useless to devote time and labour to attempts to precipitate pure ammonium molybdophosphate from solutions containing lime, iron, vanadium and all the rest; it is an unrewarding exercise to argue about the best conditions for the titration of nickel with silver nitrate and cyanide; it is lost labour to go on endeavouring to determine small traces of copper in presence of cobalt with diethyl-dithiocarbamate years after Hoste has discovered that $2:2'$-diquinolyl is specific for copper. We should be much more courageous in dropping hoary old methods and using new ones. How many British chemists use Lang and Furstenau's volumetric method for iron?[7]

A development that is as interesting as the new reagents is the increasing use of non-aqueous solvents, instead of water. These solvents are used in two ways, as a medium for volumetric titrations and for extracting various substances from aqueous solutions. Actually, neither is new. Alcohol has been used as a solvent for fats, and mixed with toluene as a solvent for many oils, before titrating the weak organic acids that they often contain, partly because these substances are not soluble in water and partly because it is easy to titrate weak acids in alcohol, with phenolphthalein as indicator, but to-day there is increasing use of non-aqueous solvents in volumetric analysis, for example, glacial acetic acid. We usually think of acetic acid as a weak acid soluble in water, but we can think of it as an amphiprotic solvent that can behave in two ways—

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$
$$CH_3COOH + H^+ \rightleftharpoons CH_3COOH_2^+$$
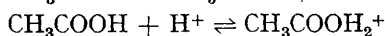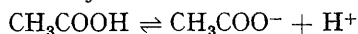
It can either donate or accept a proton, just as water behaves in two ways—

$$HOH \rightleftharpoons H^+ + OH^-$$
$$H_2O + H^+ \rightleftharpoons H_3O^+$$
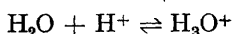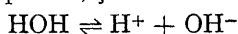
Now when a base dissolves, it can only show basic properties to the extent that protons are present for it to accept, and the more protons that are available, the more basic will

become the base. Acetic acid is far more protogenic than water, and hence the reaction $C_{10}H_7NH_2 + CH_3COOH \rightleftharpoons C_{10}H_7NH_3 + CH_3COO^-$ goes far further to the right in acetic acid than the similar reaction with water, so we can titrate our naphthylamine, as if it were a strong base, with perchloric acid in glacial acetic acid as titrant. In fact, in acetic acid all bases with $K\alpha > 10^{-12}$ are equally strong. This is called the *levelling effect*. But we may not want all our bases or all our acids to behave alike, we may want to differentiate between them. And indeed this is possible. By proper choice of aprotic, or mixtures of amphiprotic and aprotic solvents such as *iso*propanol and butyl methyl ketone, one can lengthen out the scale of acidity enormously, and potentiometrically titrate a whole string of acids or bases of varying degrees of strength, one after another.

The use of solvents as extractives is also in part an old story; everybody knows you can extract numbers of metals from water by a chloroform solution of 8-hydroxyquinoline; Smales and I during the second World War showed how by proper control of pH one could separate iron and uranium in this way. Everybody is familiar with the fact that ferric chloride can be removed from a strong hydrochloric solution with ether; auric chloride and some other noble metal halides, *e.g.*, iodoplatinous acid, can be extracted very well with ethyl acetate.

There is no completely general theory that accounts for every case, but many such extractions can be regarded as acid - base reactions, in which the salt is an oxonium compound more soluble in the non-aqueous phase than in water. I want now to call your attention to a recent development, in which the solvent is quite strongly basic, *e.g.*, a long-chain amine. For example, a toluene solution of trinonylamine will extract chromate quantitatively from an acid solution, and separate it from chromic salts, and also extracts the uranate, permanganate, ferricyanide and silicomolybdate anions.[8] A further development that may have wide applications is to form salts that are extracted into non-aqueous solvents by adding basic dye-stuffs to solutions of complex anions. The solvent extracts the dye-stuff salt, but not the excess of dye-stuff. The colour of the non-aqueous solution is a measure of the amount of anion present.[9]

But I must leave the new reagents and pass on to the physical methods, starting with electrochemistry. The oldest uses of electrochemistry were in electro-deposition and in potentiometric titration, and, although a modern analyst has a fine array of apparatus, when he is carrying out a potentiometric titration, it is in a well-established fashion. The recent development that is significant is that the titrator now records its own result, either in the form of a titration curve (volume vs. e.m.f.) or as the reading of a "burette follower," which records the volume of titrant used. Coupled to some form of automatic sampler, these apparatus can be installed on running plant, and we are a large step further towards automatic control. Actually, although automatic titrators are in use on plants, they have certain disadvantages, one of which is that they use large volumes of expensive standard solutions; the next step in this direction will possibly be an application of *coulometry*. This has been surprisingly neglected in Great Britain, but in the U.S.A. very considerable use is made[9] of it, and we should be putting more effort than we are into coulometry in this country.

There is simply not time to consider electrochemistry further; the various derivatives of polarography are making great contributions to some kinds of analysis, organic as well as inorganic, but I want to press on to the other purely physical methods, which are really revolutionising our ideas. The practice of chemical analysis has been profoundly modified during the last 30 years by a succession of improvements in detail, which we have been considering until now; what is now revolutionising our thinking in almost every branch of analysis is the possibility of chemical analysis entirely (or almost entirely) by physical means.

Many of us have been practising instrumental physical methods of analysis for years without being aware of it. Determining a refractive index in the course of the analysis of a fatty oil is just as much an instrumental physical method as determining the optical density of a hydrocarbon at a wavelength of $14\,\mu$. The difference is that in the second example the apparatus is much more expensive.

There are two reasons for the increasing use of the more expensive "instruments" in an analytical laboratory (1) because you cannot obtain the desired results in any other way and (2) because you can obtain the results quicker; the combination of these two reasons has enormous persuasive power. The kind of instrument that I now want to describe usually—but not always—includes some stage of electronic amplification, and it is a most striking tendency of the present time that very often the final result is displayed as an electrical signal. This

is important outside the laboratory, as well as inside, because an electrical signal may perhaps be amplified and used to control a process, or, if not, may be displayed on a dial or chart so that the process operative can see it and act on it without having to wait for a sample to be taken to a laboratory, analysed and reported on. In the first case, the analysis is almost instantaneous and often continuous, in the second the delay must be appreciable; in a modern continuous process this can make the difference between success and failure. The increasing industrial use of infra-red measurements to control processes is a good example of successful application. This is but one instance of the rapidly expanding use of spectrophotometers in industry. In principle there is no difference between absorption analysis in the ultra-violet, the visible or the infra-red region of the spectrum; we think they are different because in the visible region we can perhaps regard a spectrophotometer as a legitimate descendent of a row of Nessler jars, and because the means of detection of radiation is different in the three cases. But what we do in each case is to measure radiation at a particular wavelength in order to ascertain how much passes through a particular solution; in fact, we measure transmission, but think in terms of the logarithm of the absorption.

Use of these instruments has had three very marked effects. First of all it has made readily accessible to us for measurement properties of the greatest analytical importance and so made possible many analyses that would formerly have been prohibitively complicated; e.g., it is difficult to imagine the production of pure p-xylene as possible without the determination by infra-red absorption of the individual xylenes in hydrocarbons. Secondly, the use of monochromators has enabled many inorganic determinations to be made photometrically without recourse to chemical separations (for example, copper in presence of chromate or vice versa). Thirdly, it gives us a new and accurate method of determining a vast variety of organic and inorganic compounds for which slower methods were already known.

Now what accuracy can we obtain by this system? If it were low, we could use the method only for relatively small percentages, or for analyses of a low order of accuracy, and until quite recent years this was the view almost universally held. But it is not correct. Under favourable conditions one can measure radiation to an accuracy of about 2 per cent. of the amount present, that is, an error of not much more than 0·2 per cent. would be expected in a sample containing 10 per cent. of a component. But by measuring differentially, that is, measuring the difference between the sample and a known standard, vastly better accuracy can be attained. For example, phosphate can be determined by measuring differentially the colour given after converting the phosphate to $H_3PO_4VO_3.11MoO_3$, and on a fertiliser containing 12 per cent. of P_2O_5 the standard deviation is only 0·03; amazingly good for a routine measurement. In the analysis of aromatic hydrocarbons for o- or p-xylene, the error by infra-red analysis is only about 0·2 in 20 per cent.; 15 years ago an honest analyst reported an infra-red analysis as 20 ± 5 per cent.

Besides being quick and accurate, spectrophotometry in some cases gives us both sensitivity and specificity. It also readily lends itself to being combined with other techniques, such as chromatography. For example, in the determination of polynuclear hydrocarbons in the atmosphere, careful chromatographic fractionation is followed by final spectrophotometry in the near-ultra-violet region, preferably with a recording instrument.

I must at this point diverge and say something about chromatography—one of the brightest jewels in the modern analyst's crown. Invented—I think that is the word—many years ago, vastly modified by Martin and James. Dozens of analysts, employed in analysing hydrocarbons, esters, alcohols, phenols and essential oils, now wonder how they ever used to do their work before they had this technique. There is no time to say much about the older forms of chromatography, or the fascinating uses of ion exchange in inorganic analysis, but I must mention that revolutionary development—gas-phase chromatography. This is not the occasion to give any detailed description. The travelling gas behaves like the flowing liquid in ordinary partition chromatography and mixtures of volatile substances are separated in a manner analogous to the separation of carotenes and chlorophyll in the analysis of leaf pigments. In a few years devices of quite fantastic sensitivity have been made to determine the separated components as they flow from the column, so that on a sample of a cubic centimetre or so of gas—say mixed hydrocarbons—one can detect and determine as little as a few parts per million of some particular component. Development in the art of selecting suitable stationary phases has progressed so far that there are now few mixtures of volatile liquids—say with boiling points up to 300° C—that cannot be wholly or partly resolved and

hence analysed by this means, often in the space of a few minutes.   Alcohols, esters, fatty acids, halogenated hydrocarbons, all are readily and quickly analysed by this method.

It is commonplace to analyse the C_2 to C_4 fraction from a petroleum cracker, containing as many as 11 or 12 hydrocarbons, in 20 minutes or less, and the sum of the results for each component will be between 98 and 102 per cent.   This is more accurate than mass spectrography, quicker, simpler and cheaper.   In fact, I venture to say there would be few mass spectrographs in oil refineries if vapour-phase chromatography had appeared 10 years earlier than it did.

A similar remark could be applied to X-ray fluorescence analysis as a possible replacement for emission spectroscopy in the inorganic field.   But the story of the application of emission spectrography to analysis is extraordinarily interesting and illustrates so many points that it is worth while to spend a few minutes over it.   Not the least interesting is that, although the first application of the method to chemical analysis was in 1826, it was not applied to the regular analysis of any product for another 100 years.

In many recent applications of physical techniques, the development of usable apparatus has rapidly followed the first academic indications that a property could be measured, but in spectrography many years elapsed before readily usable apparatus was made, and even then it was a long time before the method came into regular use.

The first real spectroscope was made by Fraunhofer, who in 1817 combined a slit, a crown-glass prism and a theodolite.   In 1826, Fox Talbot, the inventor of photography, wrote a paper on "Some Experiments on Coloured Flames," in which he examined with a prism and a slit the *red fire* used in theatres.   It gave a beautiful spectrum with many bright lines.   Talbot wrote "The red ray may be the effect of strontia, since Mr. Herschel in 1823 found in the flame of muriate of strontia a ray of that colour.   If this opinion should be correct and applicable to the other definite rays, a glance at the prismatic spectrum of a flame may show it to contain substances which it would otherwise necessitate a laborious chemical analysis to detect."   Eight years later, in 1834, he wrote "It is difficult to distinguish the lithia red from the strontia red by the unassisted eye.   But the prism displays between them the most marked distinction that can be imagined.   The strontia flame exhibits a great number of red rays, not to mention an orange and a very definite bright blue ray.   The lithia exhibits one red ray.   Hence I hesitate not to say that optical analysis can distinguish the minutest portions of these substances with as much certainty, if not more, than any other known method."   This is the first definite statement on the possibility of spectrochemical analysis.   In 1860 there was Bunsen's paper on "Chemical Analysis by means of Spectral Observations," and in 1861 Bunsen and Kirchhoff by means of the spectroscope discovered rubidium, followed shortly by caesium.   Various other elements were first discovered by spectrographic means, and in 1874 Lecoq de Boisbaudran[10] published an atlas of spectra and wrote as the opening words of the text *"Le spectroscope est maintenant l'auxiliare indispensable de tous les chimistes."*   This was manifestly not true, as most chemists assiduously neglected this aid.   Perhaps the method was too sensitive; until electricity was readily available the technique was difficult; until photography was applied later in the century, the important ultra-violet spectrum was inaccessible, and the complex spectra of transition elements could not be handled.   But in 1904, Hilger's had evolved the constant-deviation spectrograph, in 1909 the first convenient photographic medium-size spectrograph appeared, and then in 1912 the large-quartz spectrograph in very much the form that we know it to-day.

It may be said that with this last instrument the modern spectrograph arrived and really rendered quantitative spectrographic analysis possible.   I have included the above abridged history because it is interesting as illustrating the number of practical steps between the first idea and the realisation.   Not less interesting—and this is more difficult to understand—is the apparent reluctance with which all except a very small handful of enthusiasts —Ramage, Hartley, de Gramont—greeted the "new" method.   In 1923 de Gramont was almost alone in using spectrographic methods for quantitative analysis—and apparently his apparatus was not provided for him by his university, but bought out of his own pocket. There are probably three reasons for this slow appreciation of the possibilities of this method. Very few analysts had the academic background to realise what it was that they were being offered, because this was the first such technique to appear, and the underlying ideas were too foreign to their life.   Secondly, there were already more or less adequate ways of analysing most commercial materials; after all, we made and analysed copper, alloys and steels long

before spectrographs became available.   Thirdly, the instruments at first sight appeared to be expensive, and—as some of us can remember too well—laboratory assistants were cheap.

In another 10 years, however, the picture was different.   To quote the A.S.T.M. bibliography on spectrochemical literature "the contagion quickly spread through the civilised world and papers appeared in many languages," and the cause was the rapidly increasing scale of metallurgical operations, which necessitated more and quicker tests to control products sold to more and more exacting specifications.   By 1923 one brass foundry in the U.S.A. was using a spectrograph qualitatively, and shortly afterwards routine checks on the purity of zinc and cadmium were being carried out in Norway and Belgium.   In England, Main-Smith wrote an important paper in 1934 on applications of spectrography in the non-ferrous metal industry, but its use for quantitative control of both light alloys and copper had been well established at I.C.I. Metals by 1931.   In 1930 Twyman and Fitch read a paper—the first in English since 1875—on ferrous metal analysis.   They described the use of a logarithmic sector, so that the *length* of the line is related to the amount present, and plotted the lengths of, *e.g.*, a nickel line against the amount of nickel in a series of standard samples.   In 1933 a second paper by Twyman appeared, dealing with the determination of Ni, Cr and Mn by the internal-standard method.   This important paper was read at a meeting of the Iron and Steel Institute at Sheffield, and it would be a salutary exercise for all analysts to read the discussion.   Perhaps only the authors realised that they had announced the end of an era —the era in which only chemistry was of consequence in industrial inorganic analysis. Twenty-six years afterwards one wonders how much longer chemistry will be regarded as the dominant partner.

It was a great step forward when it was firmly established that the ratio of the intensity of a suitable iron line and of a suitable line of the alloying element were logarithmically related.   These intensities are estimated by measuring the darkness of the lines on the photographic plate, and even after good microphotometers were produced about 1939 or 1940, accuracy was not very high, partly because of the nature of the photographic plate, and considerable ingenuity has been shown in devising expressions that would, so to speak, straighten up the curved graphs obtained and make them into straight lines.   After 1939 excellent optical instruments were produced with which standard spectra and the spectra from samples could be projected and compared side by side and selected lines in the spectra measured in a microphotometer.   If necessary, this microphotometer can be coupled to a recorder and the optical densities of a whole series of lines recorded one after another automatically.   That is probably as far as we are likely to go for some time in photographic analysis of emission spectra.   The accuracy attainable is still not very high, perhaps, at best, 5 per cent. of the amount present.   This is adequate for smaller amounts of alloy elements and what are called *residual elements*, but is rather inadequate for the accurate determination of major alloy elements.

In the United States this process was not regarded as quick enough and a vast amount of work was put into the manufacture of spectrophotometers that would simultaneously determine a number of elements.   This is done by mounting a series of slits round the exit circle of a very large grating spectrometer.   Each slit is mounted at the point where a particular line emerges and behind each slit is a photomultiplier tube.   Thus, some suitable line of the iron spectrum is chosen as the master reference line and a series of lines, one for each element required.   The instrument electronically compares the intensities of the various lines with the iron line and can present the results either as lines on a bar chart, which give the ratios of the elements to iron, or it can even type out the percentages of elements present so that the entire analysis of the specimen can be presented in a few minutes once the instrument has been bought, installed in a thermostatted room and calibrated.   Numbers of these expensive and complicated instruments have been made in England and are in use in the ferrous and non-ferrous metal industries and in the uranium industry.   Of course, this instrumentation does not really get over the inherent difficulties of the emission spectrographic method.   It is still one of the less accurate methods of analysis and it is rather curious to note that progress in emission spectrography is now most conspicuous in a form of spectral analysis that thirty years ago seemed moribund—flame photometry.   In suitable instruments —which need not be too complicated—it is surprising what accuracy can be achieved; for example, by using the method known as "close bracketing" (a kind of differential method) one can determine potash in fertilisers, up to 20 per cent., as accurately as by platinic chloride. For some unexplained reason accuracy falls off above the 20 per cent. level.

Besides increasing use of sensitive instruments containing monochromators, great progress is being made in *absorption flame photometry*, which is almost specific for the element in question and is more accurate than emission flame photometry. The latest development is use of a *very* hot flame of cyanogen burning in oxygen; not the sort of thing I feel I should like to have in my own laboratory, but it may develop further.

But I want to pass on to the most important development in inorganic analysis for many years—X-ray methods, and particularly the use of X-ray fluorescence.

The earlier methods of X-ray analysis followed the general line of bombarding the sample with a concentrated stream of electrons so that it emits the X-rays characteristic of the elements contained. These were diffracted at a crystal surface and recorded. The method was difficult; the sample had to be pasted on to the target of an X-ray tube, which then had to be pumped down, and it never attained any great popularity, though undoubtedly it was of great use from time to time. At the same time, say from 1935 to date, the use of X-ray diffraction crystal analysis steadily increased, and it is not difficult to see why it should. To take the simplest possible instance—if an analyst is asked to analyse a mixture of sodium sulphate and potassium chloride, he can by chemistry determine the sodium, the sulphate, the chloride and the potassium. He can then go on to do some calculations that lead him to the conclusion that what he has is sodium chloride and potassium sulphate, or sodium sulphate and potassium chloride, but these calculations break down if several other salts that contain the same components are present or if the salts are present in molar ratio, and it may well be that the real interest in the sample is not in how much chloride, how much potassium and how much sulphate it contains, but in the simple question "Is this potassium chloride and sodium sulphate or is it potassium sulphate and sodium chloride?" The analyst, if he were ingenious and possessed a polarising microscope which he knew how to use *might* be able to answer this question. The X-ray crystallographer with a diffraction camera could answer it categorically and fairly quickly. This, of course, is an absurdly simple example; the real value of the technique is usually in far more complicated cases. For example a firebrick consists of 90 per cent. of silica and has been heated. Above a certain temperature the silica will have been converted to tridymite, which can be identified readily by X-ray diffraction, but probably by no other means, and it may be very important to know to what temperature the firebrick has been heated. A pigment may be largely titanium oxide. The chemical analysts tell us that it contains 85 per cent. of titanium oxide. What we really want to know may be, not how much titanium oxide is present, but how much is rutile and how much is anatase, and again X-ray diffraction can tell us the answer.

In the Billingham analytical laboratories, the method is being continually used for the qualitative or semi-quantitative analysis of boiler deposits, deposits in chimneys and flues, mineral specimens and so forth. A practiced man learns to recognise at sight numerous X-ray patterns and if he cannot recognise them there is a fairly standard system of reference so that they can be identified readily from tables. After all, why should we do qualitative analysis and destroy the sample in the process when the X-ray crystallographer can tell us nearly as much in about one quarter of the time and hand us our sample back when he is finished with it? There is, of course, a catch in it, a catch of rather serious nature; in fact, there are two catches. The first is that colloidal materials give no indication to the X-ray crystallographer at all of their nature and the second is that there may be ambiguity if too many related crystal forms are present. There was, some years ago, a dreadful case when after examination by X-ray diffraction a flue dust was said to consist of zinc oxide. This so surprised everybody that we were asked to resort to good old-fashioned wet analysis to find out what the stuff really was. It was mostly amorphous carbon, soot in fact, and it contained about $1\frac{1}{2}$ per cent. of zinc oxide, but that being the only crystalline substance present was the only one the X-ray spectrographer could find. This is a simple example of two facts, the first of which cannot be over emphasised, that there are no infallible methods of analysis, the second—dare I mention it?—is that from time to time even quite competent analysts will commit the most frightful of blunders.

So far we have been considering X-ray diffraction and emission, but since about the end of the last War apparatus has become available that makes analysis by fluorescent X-rays very simple indeed.[12] If X-rays of very short wavelength are generated in a tube with a tungsten or molybdenum target and these X-rays are used to irradiate a sample, the elements of the sample will themselves be excited until they emit so-called secondary or fluorescent X-rays. They are called fluorescent X-rays because the phenomenon is almost exactly

analagous to fluorescence as ordinarily understood. When irradiation of a molecule by light of fairly short wavelength causes the molecule to emit light of a longer wavelength, the wavelength of the emitted light is characteristic of the compound in question and, in the same way, the wavelength of the secondary or fluorescent X-ray is characteristic of the element in question, because here we are dealing not with a molecular property but with an atomic property; thus it does not matter under what sort of combination the atom finds itself it always emits rays of the same wavelengths. The number of possible wavelengths for each element is quite small. These rays can be collimated and diffracted at the surface of a crystal mounted in a goniometer. The angle of diffraction of the beam of X-rays will depend on their wavelength and their wavelength depends on the atoms present, so that measuring the angle of diffraction will tell us what elements are present and the amount of X-rays at the particular angle will tell us how much of each element is present. We can thus make a qualitative and quantitative analysis of our sample by means of fluorescent X-rays. It is also interesting to know that here we have another physical method of analysis that is independent of the weight of the sample, because as long as the same area of sample is exposed to the beam of primary X-rays and the sample is so thick that no X-rays pass right through it, the same amount of secondary X-rays will always be produced. The sample may be powdered or it may be in solution or again it may be a homogeneous solid, such as a glass or cast metal; it makes very little difference. Once the calibration has been made it is possible to do an analysis of, for example, a catalyst for its heavy-metal content in no more than 3 or 4 minutes. The procedure is to measure the intensity of the X-rays diffracted at the angle peculiar to the element in question by means of a Geiger counter or scintillation counter and determine the amount of X-radiation emitted in a given time. Another interesting point about this system of analysis is that it can be made independent of chemically analysed samples—in some cases. If the sample is a solution or a suitable powder one can add a known amount of the element in question and again determine the number of counts at the proper angle. A little arithmetic then tells us from the ratio of the two counts how much of the element was originally present. But in general it is usual to calibrate the instrument with analysed samples; indeed, once again, somewhere behind the magnificent array of electronics, scintillation counters, dials, power packs, recorders and all the rest of it, somewhere in the background there is a chap, usually (I regret to say) nowadays in his middle-age, who knows his periodic table and knows the classical methods of analysis and knows how to use his hands, and as far as I can see it is still going to be some time before we can get away from him. Unfortunately, *he* is usually middle-aged, and it is apparently one of the most difficult things in the world to train his successors, and here is one of the analytical administrator's perpetual problems.

A fairly eminent American chief analyst said to me some time ago, "20 years ago if I were given a can of paint on a Monday morning, by Wednesday morning my boss expected to know the mineral constituents of the pigment, what oil had been used, and the nature of the thinners. Nowadays if I give a man a can of paint on Monday, by Wednesday morning he has not even decided what wavelength to use." This is really unfair because the can of paint at the present day is a vastly more complicated business than the old linseed oil - turpentine - mastic mixture that my acquaintance had in mind, but as a man who sometimes wants the analysis of an out of the way sample in a hurry I do indeed sympathise with his rather bad-tempered remark, and no more than he do I know how to convert a present-day graduate into a good old-fashioned "wet" analyst. (In America a "wet" analyst is one versed in the classical tradition in which considerable use is made of reactions in aqueous solution.)

I am inclined to think that in large laboratories the solution of the problem may lie in extending the importance of the standardisation section, which will have to supply a stream of accurately analysed samples to be used in standardising the apparatus that will be used for doing most of the analysis.

I must now draw to a close, conscious of the fact that I have not mentioned several important topics, such as the methods that have only become possible since atomic energy began to be available, mass spectrography, nuclear-magnetic resonance and biochemical methods. These last have up to now been used only in the pharmaceutical industry and to a limited extent in the determination of certain vitamins. But if, as seems likely, the practice of adding potent bacteriostats and other biologically active substances to feeding-stuffs continues as part of the ever-intensifying effort to increase the productivity of agriculture, we may see their use increasing in fields where a few years ago they were almost unknown.

Nor have I said anything about another important influence on progress in chemical analysis—that is the increase in so-called "standard" methods of analysis, and here before I conclude I must make one or two observations. When we are dealing with arbitrary or empirical methods of examination, in which results have meaning only if they are obtained under given conditions, clearly the more closely defined the conditions the better. But this need not be true when we are determining a chemical entity. If the sample is to be analysed for arsenic, or copper, or uranium, or sulphur, the extent to which we need "standard" methods is a measure of the extent of our ignorance. I do not deny that commercial considerations make it convenient and profitable that agreed methods should be available, if only because two parties are then more likely to get the same answer and so save an expensive dispute. Lundell[5] divided the analytical population into "determinators and analysts. The determinators, who are by far the more numerous, are of two kinds. First the common determinators who follow a method exactly without knowledge or concern as to the reactions involved and second the educated determinators who can handle systems containing one or perhaps two variables . . .," and it is for these people that we spend so much time preparing "standard" methods. To the accomplished analyst determining an element in an inorganic sample, such a method ought to be unnecessary and in fact is sometimes simply frustrating. The better the analyst in charge, the better able he is to write his own methods, which will commonly be found more satisfactory for the materials he is dealing with; if the right man is in the right place, he will often find himself saying "Yes, I know it says you dissolve 0·5 g of the sample in 10 ml of nitric acid, boil for 15 minutes, and all the rest of it; *we* are going to dissolve 0·25 g in 10 ml of hydrobromic acid, add 10 g of potassium bromide, dilute to a litre and measure the optical density at 375 mμ." I will further point out—and this is a thing far too little realised—that when you have standardised anything you have done your best to stop it developing; whether you realise it or not, what you are saying is "There has been plenty of development here, let us standardise what we have now." I have done my share in standardising methods both inside our own organisation and outside it, but it is work I always regard as expedient rather than commendable, and I have often thought that time would be better spent in studying the reactions rather than in "standardising" them.

In this context I will tell you a favourite anecdote of mine about an old Dutch friend who was visiting our laboratories some years ago. We were walking along discussing analysis in general and he suddenly stopped and said "Mistaire Vilson, I vill tell you an analyst." His English was fluent but occasionally not quite grammatical. So I said "I don't quite understand, but you tell me an analyst." And his reply was absolutely to the point, "An analyst is ven zay say zere is a standard method for so and so, and he vill say, 'Ja, but I know a better von.'"

In a recent editorial in *Chimie Analytique*,[12] Professor Charlot has summarised the analytical situation as he sees it in France. Perhaps two of his aphorisms are not entirely wide of the mark in this country—

S'il s'agit de problèmes classiques, le laboratoire est en general organisé pour effectuer les opérations correspondantes. Mais aujourd'hui les problèmes nouveaux sout prépondérantes.

De nombreux analystes devraient repasser par l'École.

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