

IS RADIOCHEMISTRY THE ULTIMATE IN TRACE ANALYSIS?

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ABSTRACT

The literature of Analytical Chemistry abounds in papers describing the use of specific measurement techniques for the determination of trace amounts of both inorganic and organic constituents. Recent emphasis throughout the world on problems of pollution and health has encouraged the extension of existing trace methods and the search for, and development of, potential new techniques.

Unfortunately, it often appears that the field of trace analysis is split into two widely disparate groups: one, where proponents of a particular technique tend to measure the capabilities of their methods on 'distilled water' or other near ideal systems, and the other, where those developing the trace methods must apply them without delay to very practical samples such as air particulates, waste water, food, blood, etc. The former experimenter often extolls the 'ultra' sensitivities of 10^{-8} to 10^{-9} grammes attainable under certain conditions, while the latter often expresses satisfaction if he can get an answer on his practical sample to within an accuracy of 10-25 or even 50 per cent. Often, also, there is little communication and/or understanding between members of these two groups.

Whether we like it or not, trace analysis is today in the spotlight of public attention and the analytical chemist can perform an important service if many of his efforts can be related to the solution of some of these practical problems. Thus, when the environmentalist asks about the amount of contaminant in a specific sample the analytical chemist should be able to give an unbiased value with an associated accuracy limit—not just a value obtained with highly refined measurements using one or another specific technique or procedure.

Proponents of widely-used trace analysis methods such as atomic absorption, spark source mass spectrometry, polarography, activation analysis, etc., often give the impression that their methods alone can solve a large fraction of the problems of trace analysis. In addition, from time to time new, specialized trace methods are reported and sometimes find use in solving special analytical problems. However, the trace analyst deceives himself and, worse yet, gives false impressions to others unless he is able to understand the biases of his methods and instruments in relation to other possible methods and instruments and in addition expresses these biases quantitatively as accuracy error limits.

Our experience at NBS in certifying trace element Standard Reference Materials in matrices as diverse as glass, orchard leaves, gold, zinc, beef liver, tuna fish and coal has given us an insight into the optimum contributions which can be made by many of these methods. The advantages and dis-

advantages of activation analysis as well as of several other types of radiochemical methods will be discussed in relation to other trace analysis techniques, based on our NBS experience in practical trace analysis.

INTRODUCTION

The area of trace analysis occupies a place of primary importance in public affairs throughout the world today¹. Many decisions on the quality of the environment must be based on measurements of constituents at the sub-ppm level in air and in water. Additives to food products, either introduced during processing or absorbed in some way from the environment, must often be determined at the ppm level or below. Geochemists making measurements on components of both land and water areas require accurate measurement of traces below the ppm level. In industrial processes, such as those used in the semiconductor industry, the quest for meaningful measurement of chemical contaminants has moved from the level of the ppm to the ppb and lower, in the hopes of better understanding of materials such as silicon used for semiconductors. Even traditional metal industries such as steel have increased their interest in peripheral trace metals at levels approaching the ppm region, and uses for special high-purity materials seem to be multiplying.

Thus there is today an increasing demand for trace analytical methods of special high sensitivity that can be applied with reasonable speed, that will give good precision, and, above all, that are accurate. Because the ultimate job of an analytical chemist is to apply his methods to practical analyses, each practitioner of an individual analytical competence is faced with a realistic evaluation of his own measurement approach *vis-à-vis* other potential trace analytical methods. The purpose of this paper is to explore the general milieu in which the trace analyst operates today, and then to give my estimate of the position of radiochemistry, and more particularly of activation analysis, relative to other trace methods.

THE FIELD OF TRACE ANALYSIS

Unfortunately, laboratories doing trace analysis today generally fall into two groups. In one group, proponents of a particular method devote themselves whole-heartedly towards improvement of the sensitivity of the measurement, but at the same time pay little attention to major interferences which may occur in many practical samples. All too often these chemists are like the determinators described in a classic paper by Lundell², one of my predecessors at the Bureau. Lundell described such determinators as persons 'who can handle systems containing one or perhaps two variables, or who, like determinators of pH, are chiefly interested in group effects and make no effort to go beyond this'. He pointed out that 'the determinator's salvation lies in the development of truly selective methods of analysis, and his final resting place will be a heaven in which he has a shelf containing 92 reagents, one for each element, where no. 13 is the infallible specific for aluminium, no. 26 the sure shot for iron, no. 39 the unfailing relief for yttrium, and so on to uranium'.

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Lundell in 1933 could not have imagined the tremendous increase in sophisticated instrumentation that would be available to the analytical chemist 40 years later. But his perceptive picture of the determinator still stands. Today's determinator, however, is interested in combining a series of black boxes which, when used to analyse a simple, pure material such as distilled water, will be able to determine a particular element or compound to high sensitivity. One needs only to peruse the current analytical literature to note the variety of manuscript titles which purport to hold the key for the analysis of ppb and smaller amounts of particular important contaminants.

Unfortunately, in the last decade or two our university academic system has tended to foster this approach to Analytical Chemistry, particularly in the Chemistry Departments where the 'rough and tumble' of the practical sample is often not readily available. Indeed, at a recent symposium on trace analysis specifically directed towards practical samples, one well-known university professor began his talk with the statement that since he was at a university and had no access to practical samples he would have to confine his talk to discussions of instruments and techniques themselves!

Even in the 'Land Grant' Colleges in the United States it has been fashionable for the Analytical Chemistry Department to remain in its 'ivory tower' and let those with the real analytical problems, such as the agricultural chemists, the veterinarians, the biomedical chemists, etc., do their own analyses. Fortunately, with the changing pattern of support for universities in our country we are beginning to see a true interdepartmental approach develop in certain schools. I point to the University of Illinois as an excellent example where a number of departments are working in real co-operation on problems of lead pollution. Such interaction among disciplines can only help to improve the analytical capabilities of all.

At the other end of the scale of the analysis picture, one finds many laboratories that are completely overburdened with practical samples which must be analysed immediately. In most cases these laboratories just do not have time to spend to make significant improvements in their methods, but instead must rely on information abstracted from the literature and apply it to their own samples. Unfortunately, they often find that literature descriptions of 'new-fangled' instrumental methods reported to give the ultimate in sensitivity have little or no application to the problems which they have to solve. Often, too, they must be satisfied with methods which give 25-50 per cent or greater error. It is, however, analyses by methods such as these on which many of the environmental decisions are made today, and it is my belief that it should be a prime goal of the trace analyst to try to improve the *accuracy* as well as the *precision* of many of these methods.

THE REAL WORLD OF TRACE ANALYSIS

When I went to the National Bureau of Standards in 1963, from the academic environment of the University of Michigan, I had many plans for emphasizing trace analysis with the wide variety of techniques available at NBS. My early experience with activation analysis as well as other trace methods had shown that one of the serious problems in trace analysis was

that of reagent blanks. Therefore I very soon proposed to set up a special service at the Bureau for supplying high-purity reagents to enable analysts in the Division to improve even further the sensitivity of the ultra-trace techniques they were using.

My initial efforts met with general unconcern and lack of interest. Those working in the areas of spectroscopy, polarography, flame emission and mass spectrometry, as well as spectrophotometry, did not flock to the doors of our special custom reagent service. Indeed, we soon found that special reagents, such as those available in the late 1960s from Merck-Darmstadt and Baker, generally satisfied most of the needs of the Division. There was little need to purify our own reagents at that time except for one or two very special cases.

About the same time we initiated a program to develop Standard Reference Materials (SRMs) for trace analysis in three types of matrices: high-purity metals; trace inorganic materials, such as glasses, and trace biological materials. Because of requirements elsewhere in the Bureau for high-purity metals for temperature measurement and electrical measurement, we started work first on high-purity metal SRMs. Although considerable effort was expended on high-purity SRMs of zinc (SRM 682), platinum (SRM 680) and later gold (SRM 685)³, the general reaction in many different trace measurement areas in the Division was that these materials were *too pure*. The spark-source mass spectrometrists preferred 'doped' samples so that they could develop calibration curves. The activation analysts were able to detect only a few element in these particular high-purity metals. Other competences were not particularly interested.

Thus, the combination of low demand for high-purity reagents and the general lack of interest in certifying metals of very high purity began to impress upon me the fact that, although many of our individual trace analysts *said* that they were able to analyse at the ppb level, very few, if any, of them were really capable to analysing at much below the ppm level on *practical samples*, except under special circumstances. An extrapolation of this fact led me to a much broader conclusion that if this were the situation among experts at NBS who were reasonably accustomed to working with practical samples, then certainly few of the trace analysts throughout the world were really able to work effectively with sub-ppm amounts of contaminants in practical samples.

This general situation is further illustrated by the fact that there are almost no standard materials certified for concentration of elements below the ppm level. This indicates a high degree of difficulty in obtaining and certifying such materials and a general lack of concerted effort towards accurate measurements in this area.

In the very late 1960s I had occasion to test this hypothesis once again as we began to work on a special set of trace glasses⁴, which had been prepared as Standard Reference Materials with additions of 0.02, 1, 50, and 500 ppm of 61 different elements. Several years of effort had been required to obtain homogeneous batches of these glasses, and by late 1968 the different trace analytical competences within the Division had the opportunity to make measurements on samples of these glasses for elements which they could determine best. Special funding was available to support the work on the

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analysis of these materials so that there was some considerable additional incentive to study the trace content of these glasses over and above scientific curiosity.

After six months a summary was made of the efforts within the Division which had led to acceptable results. *Figures 1, 2, and 3* show the elements measured at that time by competences in the Division in the 500 ppm glass,

December 1969

Analysis of trace element glasses

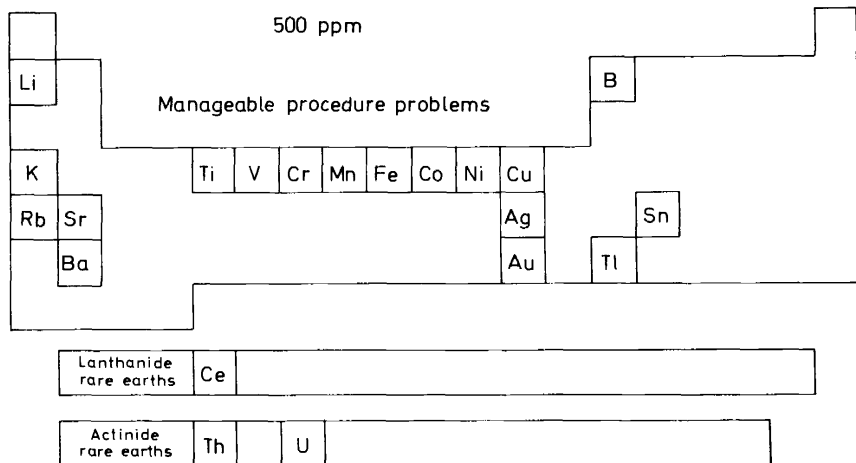


Figure 1.

December 1969

Analysis of trace element glasses

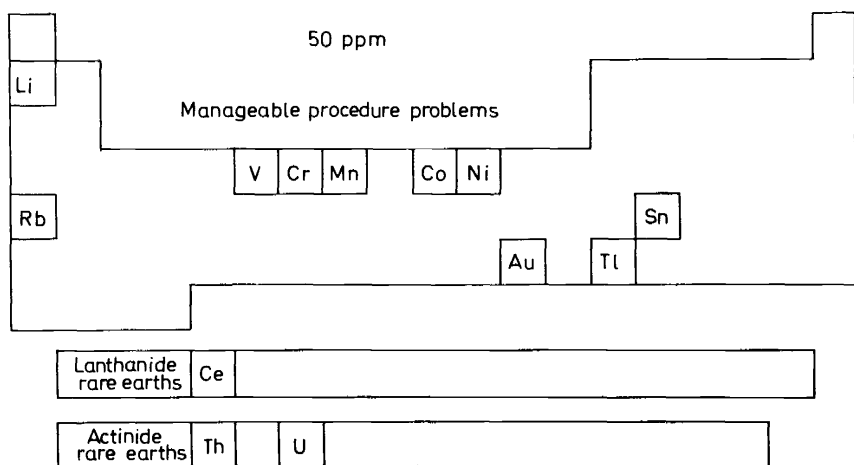


Figure 2

Analysis of trace element glasses

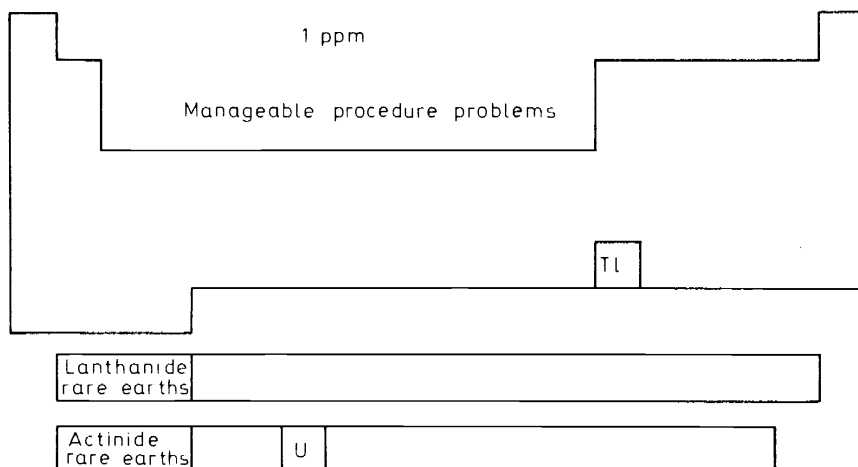


Figure 3.

the 50 ppm glass, and the 1 ppm glass respectively. This is admittedly not a quantitative exercise. Instead it is meant to give an indication of the relative order of magnitude of difficulty experienced in working at the 500, the 50 and the 1 ppm level.

It is certainly true that since 1969, in our Division and elsewhere, a large amount of effort has been expended in the certification of values for a number of trace elements at the 1 ppm level, as well as other levels. I do, however, believe that this very qualitative experiment shows that there are many more difficulties in measurements at the ppm level on practical materials, such as these trace glasses, than most analytical chemists are willing to acknowledge.

REAGENT BLANKS, HIGH PURITY REAGENTS, CLEAN FACILITIES

I would like to return for a moment to the problem of the 'reagent blank' in trace analysis. Over the past two years there has developed in our Division a demand for better reagents than are available anywhere commercially under even the highest purity specifications. This demand finally became important as our Division scientists began to cope with the problems of the 1 ppm and the 0.02 ppm glass SRM. Furthermore, in the late 1960s it was apparent that not only did the reagents used in processing contribute to sample contamination but that there was also a sizeable contamination from the containers in which the reagents were stored, as well as from the environment of the room in which the analyses were being done. When a number of semiquantitative studies indicated that some of our rooms were contributing as much as 90 per cent of the contamination in a particular blank, we considered it essential to adopt some type of clean-room operation.

Traditionally designed clean rooms, which had been used for dust control elsewhere in the Division, became inoperative when quantities of reagents were used in them. Since most ultra-trace analysis on practical samples today requires many manipulations with reagents, we found it necessary to develop a special design for a clean room. At the same time we also developed special facilities to produce very high-purity reagents by sub-boiling distillation. With these facilities and the special reagents, we have been able to lower the blanks for elements, such as lead, in reagents by one or two orders of magnitude. A paper recently submitted to *Analytical Chemistry* describes our procedures and analyses for very high-purity reagents⁵.

Thus to analyse real samples at the sub-ppm level by most trace techniques requires a large amount of care, special facilities and special reagents to reduce the influence of the reagent blank. However, activation analysis, when properly exploited, is much less affected by these particular problems and therein lies a major advantage.

CONTRIBUTION OF RADIOCHEMISTRY TO THE ANALYSIS OF PRACTICAL TRACE SAMPLES

We have now had several years of experience at NBS in applying a number of trace-analytical competences to the certification of high-purity Standard Reference Materials in metal, glass, and biological matrices. Several of these materials (e.g. the 1.0 and 0.02 ppm Trace Glasses, SRM 614, 615 and SRM 616, 617 respectively; and the Orchard Leaves, SRM 1571) have been recommended by Commission 7 of the IUPAC Analytical Chemistry Division as samples for international laboratory comparison⁶, because of their proven homogeneity. Let me describe below some of our experiences in certifying these and similar SRMs, and point out the special contributions radiochemical methods have made.

Most of the information presented on the certificate for the 500 and 50 ppm glasses has been obtained by the traditional techniques of spectrophotometry, flame emission spectroscopy, polarography, etc. It is at the 1 ppm level that activation analysis begins to make a major contribution, and when used in combination with radiochemistry the problem of reagent blank is eliminated. Of the fourteen elements which have been certified in the 1 ppm glass, activation analysis has contributed to the certification of seven and has provided useful information for other elements which have not yet been certified.

It should be pointed out here that our standard operating procedure at NBS requires that for certification of a measurement value on an SRM the measurements should have been made by two completely independent competences, or alternatively, by two completely independent laboratories using referee-type procedures. When information from only one competence or one laboratory is available, that particular value is not certified but added to the certificate in parentheses for information only.

In considering values for accuracy determinations on samples such as the 1 ppm glass, we find that when isotope dilution mass spectrometry can make the measurement it will be accepted as a referee-type method if results can be obtained from two different laboratories. Thus at the 1 ppm level, this method is used uniquely for elements such as thorium and uranium because the

method has been well studied in terms of systematic errors and consequently its accuracy is well known. This is not to say that this method would be used daily in a routine laboratory. It is complicated and its development as a competence requires major effort and equipment. However, it is worth special investment of time and effort to certify Standard Reference Materials that subsequently can be used for calibration in laboratories throughout the world.

At the 0.02 ppm level of glass the radiochemical method of activation analysis really comes into its own! Note that two years after the trace glasses were first made available, there were still no certified values for the 0.02 ppm glass because few if any competences other than activation analysis had been able to reach that level of sensitivity with acceptable values. (You note here some substantiation for my cynical statement regarding the profusion of titles in the literature on 'part per billion' analysis but the dearth of applications of these methods to practical samples.)

When very special care has been taken in the use of clean facilities and ultra-pure reagents, measurements by some of the other techniques have substantiated several of the 0.02 ppm glass values during the past year, as will be shown soon with our revised certificate.

It should be pointed out that the full potential of activation analysis is wasted unless the sample is worked up radiochemically. Indeed, it is one of my pet peeves that so many people try to do so much non-destructively by activation analysis and do not utilize the truly magnificent assets of this method combined with radiochemistry.

As a matter of fact I would go so far as to propose a new term, *activation spectrometry*, to describe a variation of activation analysis in which a sample is irradiated and then directly measured non-destructively by spectrometry, without chemical processing or manipulation. As I see it, there is no difference between this approach and measurement by emission spectrometry or mass spectrometry, where the sample is excited and spectrometers are used to discriminate one component from another. This activation spectrometry suffers from all of the errors and problems inherent in the other types of 'spectrometries'. Only when radiochemistry is introduced between the nuclear activation and the spectrometric measurement would I call it *activation analysis*.

Several other NBS Standard Reference Materials in the biological field have been developed in the past year and a half. These include Orchard Leaves (SRM 1571), freeze-dried Bovine Liver (SRM 1577) and Coal (SRM 1630) samples⁷. In each of these SRMs, activation analysis has played an important role in certification of elements such as arsenic, boron, manganese, mercury, copper, zinc, etc.

A particularly illuminating story, to give perspective to the utility and general importance of activation analysis at 0.1 ppm levels, can be told about the *certification of mercury* in the orchard leaves. In January 1971 newspapers in the United States carried scare stories about the amount of mercury found in tuna fish, and later, swordfish and other agricultural products. During the first few months of 1971 organizations such as the U.S. Food and Drug Administration were heavily involved in the analysis of mercury in these foodstuffs.

The two main competing techniques in this analytical effort were activation analysis and atomic absorption. Rumour has it that literally thousands of samples were being measured by the Food and Drug Administration for mercury by atomic absorption and many hundreds by activation analysis, and that although results obtained from each technique clustered around certain values, the techniques in general varied from one another by as much as 20 or 30 per cent. Dunlap even goes so far as to suggest a 50 per cent or greater correction be made to atomic absorption values reported for mercury⁸.

Although at the time NBS did not have a meat or fish Standard Reference Material⁹ for certification of mercury, we did have available a special SRM of dried Orchard Leaves certified for a number of other elements, and we decided to certify it for mercury content as well.

Naively, I felt that this should be a rather simple task with experts in both activation analysis and atomic absorption within the Division and other backup competences to support them if necessary. Thus I assigned to activation analysis and atomic absorption the task of certifying the amount of mercury in the orchard leaves within about two months, and settled back to wait for the results! Much to my dismay results at the end of two months varied by at least as much as the rumoured variation of the Food and Drug Administration scientists! Obviously what was needed was for each group to go back to the laboratory and concentrate more heavily on its analysis. A month or two later our numbers still varied by as much as 20 to 30 per cent and everyone was painstakingly going through his individual procedural steps looking for biases.

By this time I felt it was very important that we certify the mercury in the orchard leaves to within about 5 per cent and I called upon two other competences in the Division: spectrophotometry and isotope-dilution spark-source mass spectrometry. All four competences were given specific instructions to make an all-out effort during the coming month. Weekly briefing sessions were set up to exchange information, and by the end of the month we *were* able to certify the mercury value to $0.155 \text{ ppm} \pm \sim 10$ per cent on the basis of results from activation analysis¹⁰ and atomic absorption¹¹, with substantiating values from the other two methods.

It was during this baptism in the heavy metal determination in biological matrices that I came to realize the absolute necessity for having standard materials certified for trace elements to be used to standardize methods in different laboratories. NBS invested over $1\frac{1}{4}$ man years of effort in that mercury certification and utilized four different competences in developing that certified value. Few other laboratories have the resources to attempt such an intercomparison and therefore must rely either on their own best estimates and procedures or on some referee-type standard material available to them.

Experiences such as this mercury certification have impressed upon me the fact that activation analysis, particularly when used with radiochemistry, is the least biased in providing reliable referee-type information at the 0.1 ppm level. But having made this statement, I now need to qualify almost every word. To derive optimum advantage from activation analysis it is essential that the sample be placed directly into the reactor for activation with a very minimum of handling—without the drying or other preparation

that often in practice precedes measurements called activation analysis. If the preliminary stages of the preparation of the sample for activation analysis consist of dehydrating the sample and driving off not only the moisture but some of the other low-boiling products, as is done in atomic absorption, then the methods are surely not independent and many of the errors inherent in one will be duplicated in the other.

We have recently had experience in the unique use of a radiochemical method to measure trace elements in a *lunar sample*¹². These measurements were carried out primarily by the mass spectrometrists in our Division and resulted in highly accurate ratios of uranium isotopes, lead isotopes, strontium/rubidium ratios, etc. At the same time, however, the concentration of a number of trace elements was determined by isotope-dilution mass spectrometry in conjunction with standardization by the trace-glass SRMs mentioned above. Because mass spectrometry gives measurement accuracies to within 0.25 to 0.5 per cent of the true value, much better than activation analysis, this competence was used for many of the trace elements. Polarography added several others, such as iron and titanium.

However, a novel radiochemical method, nuclear track counting, was used to determine the elements uranium and boron, which are very difficult to measure by almost any other technique. Because the nuclear-track method¹³ has been standardized and shown to be consistent on comparison with isotope-dilution mass spectrometry for the elements thorium and uranium in trace glasses, we had confidence in its values for uranium and boron.

I have not mentioned some of the other potential radioisotope methods which are reported from time to time in the literature. Indeed, 15 years ago when I was preparing the reviews in *Nucleonics* for *Analytical Chemistry* I perhaps was much more alert to the totality of the literature involved in these methods. Now, on the other hand, as I have seen the difficulty inherent in the practical sample, I must admit to a degree of cynicism as to the validity of many of these speciality methods at this ultra-trace level of the sub-ppm.

Several years ago we made a valiant attempt to apply sub-stoichiometric radioisotope dilution to the sub-ppm level of analysis for some SRMs. We just were never able to make it competitive with other trace methods below the ppm level. We did develop procedures for elements such as iron and cobalt at the 100 ppm level for certification of SRMs, but we never were able to utilize the technique below the ppm level.

It is certainly true that radioactive tracers can trace the reaction of a few atoms, but once again in practical situations it appears to be very difficult to design experiments to provide appropriate accurate analytical information. I have purposefully avoided discussing trace organic analysis. We have had much less experience with it and I do not see radioactivity making major contributions here. We have seen sensitivities increased by several orders of magnitude for organic compounds of special interest, but radiochemistry does not appear to offer important advantages.

SUMMARY

In summary then what do we see as we look at radiochemistry in terms of trace analysis? We certainly do not see a broad survey method comparable to emission spectroscopy but operating in the tens and hundreds of nano-

grammes region. We do not see a method that is particularly rapid, although certain procedures using nuclides with very good detection characteristics can be automated rather readily. In addition we see a method which is oriented almost exclusively towards inorganic trace analysis rather than organic trace analysis.

But we do find that it does have considerable usable sensitivity, indeed much more than most methods for practical samples. This sensitivity is, of course, greatest when full advantage is taken of the 'no reagent blank' asset, in other words when radiochemistry is added to activation spectrometry to make true activation analysis.

Perhaps the biggest advantage of activation analysis is that it is inherently an accurate method. Its precision may often be only the order of a few per cent, but when full advantage is taken of all of the unique attributes of activation analysis, it should also have accuracies on the order of a few per cent, even at levels approaching the 1 to 10 nanogramme level.

From our very practical experience at NBS of certifying trace elements at the 0.02 ppm level, activation analysis is the 'target' method. It is the only method that is completely at home at these levels; other methods must specially optimize their parameters in order to compete with or to match values by activation. This is not to say that activation methods can be accepted without question. We do not yet have the experience or the confidence to say that radiochemical activation methods are in the class of referee methods, such as certain isotope-dilution mass spectrographic methods. However, it is certainly true that activation methods are the methods 'to beat' at this level.

Finally, I would like to emphasize once again the fact that in practical samples from the polluted environment, from solid state physics, from biology and nutrition, or from oceanography, trace analysis imposes rigorous conditions on its practitioners. It takes extensive clean facilities, high-purity reagents, and low-level manipulation experience these days to work at the ppb level for lead, for copper, for silver, for calcium, etc. Anyone who hopes to get reasonably accurate numbers on these elements even at the 0.1 to 1 ppm level must have his blanks under control at the ppb or lower level. This means working in clean rooms—indeed, working in clean suits—where not only the environment of the room, but also the contamination the individual introduces into the atmosphere, is reduced. It means working with specially purified reagents that are orders of magnitude better than the best materials available commercially.

I maintain that very few people are really willing to work meaningfully at this low level at the present time, even though the plethora of papers in the literature describing applications of this or that new measurement technique to trace analysis seems to indicate otherwise.

Thus, when we ask what is the potential for radiochemistry in trace analysis, we find that one radiochemical method, activation analysis, eliminates or greatly reduces this contamination problem, and is able to compete very favourably at the low levels of concentration.

While one would hesitate to say that any method of analysis is the ultimate in trace analysis, it is certainly true that activation analysis applied at its full potential can lead the way in trace inorganic analysis of many elements.

REFERENCES

- ¹ W. W. Meinke and J. K. Taylor, editors, *Analytical Chemistry: Key to Progress on National Problems*. Proceedings of the 24th Annual Summer Symposium on Analytical Chemistry, NBS Spec. Publ. 351, U.S. Government Printing Office, Washington, D.C. 20234 (1972).
- ² G. E. F. Lundell, *Ind. Eng. Chem. (Anal. Ed.)*, **5**, 221 (1933).
- ³ Certificates of Analysis (Provisional): High-Purity and Doped Platinum, Standard Reference Materials 680 and 681 (December 28, 1967); High-Purity Gold, Standard Reference Material 685 (September 26, 1968); High-Purity Zinc, Standard Reference Material 682 (July 9, 1968; revised February 1, 1971). Available from the Office of Standard Reference Materials, National Bureau of Standards, Washington, D.C. 20234.
- ⁴ Certificates of Analysis (Provisional): Trace Elements in a Glass Matrix, Standard Reference Materials 610 and 611 (Trace Element Concentration 500 ppm); 612 and 613 (Trace Element Concentration 50 ppm) 614 and 615 (Trace Element Concentration 1 ppm); and 616 and 617 (Trace Element Concentration 0.02 ppm) (August 5, 1970). Available from Office of Standard Reference Materials, National Bureau of Standards, Washington, D.C. 20234.
- ⁵ E. C. Kuehner, R. Alvarez, P. J. Paulsen and T. J. Murphy, *Anal. Chem.*, **44**, 2050 (1972).
- ⁶ Recommendation, Analytical Chemistry Division, Commission 7, International Union of Pure and Applied Chemistry, Comptes Rendus, XXVI Conference July 1971, p. 191, Washington, D.C. (1972).
- ⁷ Certificates of Analysis (Provisional): Orchard Leaves, Standard Reference Material 1571 (October 1, 1971); Bovine Liver, Standard Reference Material 1577 (April 15, 1972); Trace Mercury in Coal, Standard Reference Material 1630 (November 3, 1971). Available from the Office of Standard Reference Materials, National Bureau of Standards, Washington, D.C. 20234.
- ⁸ R. Dunlap, *Chem. Eng. News*, p. 22, July 5 (1971).
- ⁹ Certificate of Analysis (Provisional), Albacore Tuna, Standard Reference Material 1578 (in process). Available from the Office of Standard Reference Materials, National Bureau of Standards, Washington, D.C. 20234.
- ¹⁰ H. L. Rook, T. E. Gills and P. D. LaFleur, *Anal. Chem.*, **44**, 1114 (1972).
- ¹¹ T. C. Rains and O. Menis, *J. Assoc. Offic. Anal. Chem.*, submitted.
- ¹² I. L. Barnes, B. S. Carpenter, E. L. Garner, J. W. Gramlich, E. C. Kuehner, L. A. Machlan, E. J. Maienthal, J. R. Moody, L. J. Moore, T. J. Murphy, P. J. Paulsen, K. M. Sappenfield and W. R. Shields, *Geochim. Cosmochim. Acta*, Supplement 3, **2**, 1465 (1972).
- ¹³ B. S. Carpenter, *Anal. Chem.*, **44**, 600 (1972).