

# A METHOD FOR THE DETECTION OF MERCURY BY RADIOACTIVATION ANALYSIS

K. LJUNGGREN\* and T. WESTERMARK

*Royal Institute of Technology, Stockholm, 70, Sweden*

Une méthode d'analyse par radioactivation est présentée, laquelle a été utilisée pour la détermination du mercure dans les échantillons biologiques, l'aluminium, la cellulose et les grains traités par des composés de phenylacetate de mercure. Une des difficultés rencontrées dans cette expérience est due à l'évaporation du mercure dans le réacteur. Cette dernière a été vaincue en scellant les échantillons dans des ampoules de quartz standardisées.

A method which has been developed by Westermarck and Sjöstrand<sup>1,2</sup> in Sweden, has been used for the determination of mercury in biological samples, aluminium, cellulose and grains treated with mercury-phenylacetate compounds. In the last two cases the method has competition from the highly developed flame method, but will possibly be of value for confirmations. In the first two cases the activation analysis method is valuable.

In activation analysis of mercury by means of neutron irradiation one has to choose between measurements on  $^{203}\text{Hg}$  and  $^{197}\text{Hg}$ . The former has a half-life of 48 days and the latter of 25 and 65 h, respectively, in two isomeric states. The use of  $^{197}\text{Hg}$  can be shown to give a sensitivity 50 times that for  $^{203}\text{Hg}$  for a one-week irradiation. The latter alternative should be used only if work close to a reactor is not possible.

$^{197}\text{Hg}$  is a very favourable case for non-destructive spectrometric determination. The 65-hour isomer which has a much higher cross-section than the 25-hour  $^{197\text{m}}\text{Hg}$  decays by  $K$ -capture, followed by a 77 keV gamma emission, to  $^{197}\text{Au}$ . The method has been based on the measurement of the 77 keV line which is readily detected in ordinary sodium iodide crystals, which is a great advantage. However, optimal conditions may arise with the use of wafer crystals which we have heard much about earlier in this symposium.

A unique difficulty which has been encountered in the work with mercury, is evaporation due to the elevated temperature in the reactor which in the actual irradiation positions is 40°–60°C. The temperature of the sample may be still higher owing to radiation absorption. Even when the mercury has been treated with hydrogen sulphide, it does not remain quantitatively in the cellulose at higher temperatures.

A quartz ampoule technique has therefore been devised. The samples and the standards, which consist of mercuric chloride treated with hydrogen sulphide, are enclosed in quartz ampoules which are sealed while the sample is protected by cooling. The spectrometry is carried out without opening the quartz containers. The induced activity in the quartz is therefore of importance. It has been found possible to measure the mercury line without interference if an ageing period of two days is used. After this

\* Present address: Isotope Techniques Laboratory, Stockholm, Sweden.

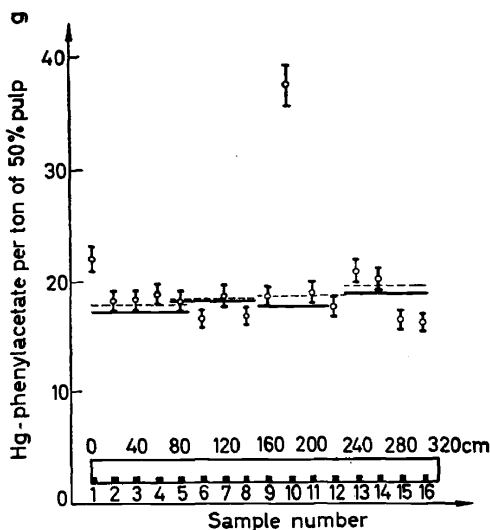


Figure 1. Amount of mercury-phenylacetate in samples taken across pulp bed determined by activation analysis (°) and chemically (--- and —)

period silicon and sodium activity from the quartz, and sodium and often copper and manganese from the sample, have decayed sufficiently.

By this method mercury has been determined in mechanical pulp (Figure 1); individual grains; brain and liver tissue from (living) rabbits exposed to mercury-containing atmospheres; human faeces (exposure of industrial workers to mercury); aluminium in corroded form; samples of the remains of King Erik XIV who died in 1577.

The sensitivity limit of the method in its present form is  $0.03 \mu\text{g}$  with a precision of 5–15 per cent after irradiation for 3 days at  $1-2 \times 10^{12}$  neutrons  $\text{cm}^{-2}\text{sec}^{-1}$ . The method has been checked by analysis of a series of prepared samples (Figure 2).

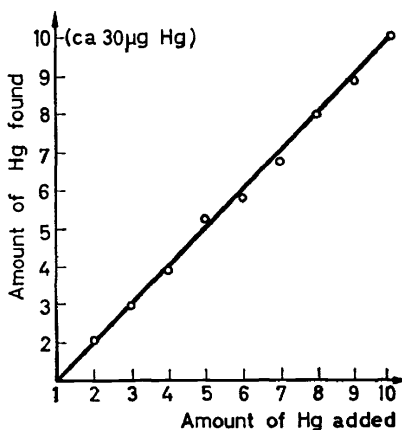


Figure 2. Accuracy test for activation analysis method  
Relative units: 1 unit  $\approx 3 \mu\text{g}$ .

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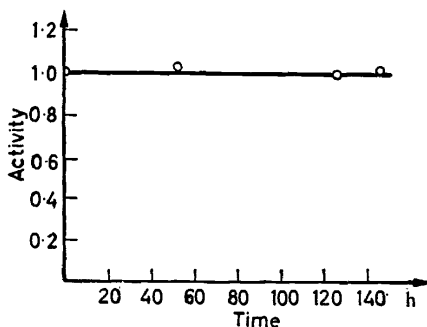


Figure 3. Activity of peak attributed to mercury relative to mercury standard against time after irradiation

Considerable experience has been gained with the method in that several hundred samples have been analysed. Difficulties due to  $^{32}\text{P}$  bremsstrahlung were encountered in attempts to analyse bone from humans. This may possibly be overcome by the subtraction method as it has been applied in similar cases by Dr Leddicotte.

Improvements in the method may be accomplished by the use of proportional counter spectrometry since the  $\gamma$ -line is converted to an appreciable degree. In this case the ampoules have to be opened before the measurement. In the near future the high flux of the material testing reactor R2 will become available, which will greatly enhance the possibilities of this and other activation analysis work in Sweden.

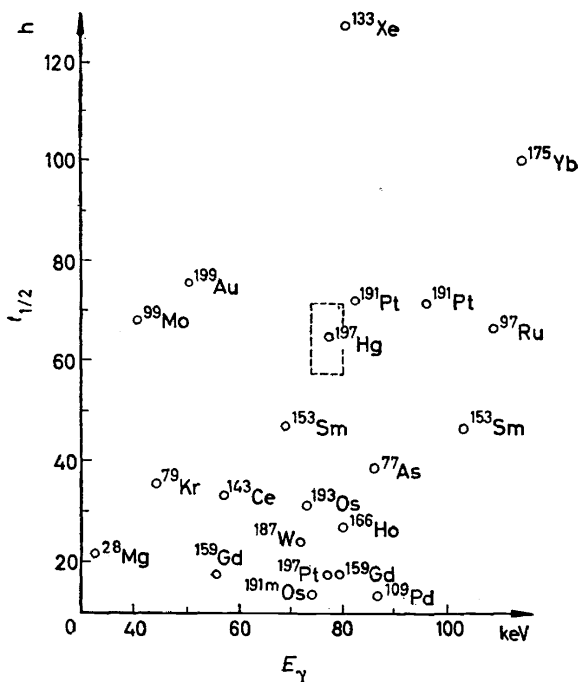


Figure 4. Part of  $t_{1/2}$ - $E_\gamma$  chart for nuclides surrounding  $^{197}\text{Hg}$

In connection with the determination of mercury in the royal remains of Erik XIV the question arose of a definite positive identification of elements present in a sample. One method of systematizing such work has been given by Westermarck<sup>3</sup>. From a series of spectra the energy of the photo-peak in question is determined together with the uncertainty in the energy. The decay of the photo-peak is followed, and compared with that of the irradiated standard. If the measured peak really belongs to the same element as the standard this ratio will be constant (*Figure 3*).

From a series of such decay measurements the uncertainty in the half-life can be obtained. Now the half-life and energy values are entered together with the determined uncertainties in a diagram which represents all nuclides produced by (n, $\gamma$ ) reactions. As is seen in *Figure 4*, the isotopes are presented as points in a diagram where energy is given as the abscissa and the half-life as the ordinate. As long as the uncertainty rectangle only contains one nuclide, and is far from others, the identification is positive.

In conclusion, the determination of cobalt in steel by means of the short-lived activity  $^{60m}\text{Co}$ , which was reported at the last Geneva Conference, has been continued on iron ores where the same method is applicable. It has been interesting to hear that Dr Meinke has also been working on this cobalt isotope. The results lie between 30 and 100 parts/million in general, but one ore has been found which contains as little as 2 parts/million. This is of very great importance indeed in the manufacture of material used in the construction of reactors where the induced cobalt activity is a great disadvantage.

## References

- <sup>1</sup> T. Westermarck and B. Sjöstrand. "Activation analysis of mercury", *Intern. J. Appl. Radiation and Isotopes*. In press.
- <sup>2</sup> T. Westermarck, B. Sjöstrand and P. O. Bethge. "Activation analysis of mercury in cellulose products", *Svensk Papperstidn*, **63**, 258 (1960).
- <sup>3</sup> T. Westermarck and B. Sjöstrand. "On the identification of gamma emitters formed by neutron activation including tables of radionuclides formed by neutron capture", *Intern. J. Appl. Radiation and Isotopes*. In press.

## DISCUSSION

A. H. W. ATEN (*Netherlands*): Has the graph of  $\gamma$ -ray energies against half-life been published?

K. LJUNGGREN (*Sweden*): The identification method will be published in the *Journal of Applied Radiation and Isotopes*.

G. W. REED (*U.S.A.*): We can confirm Dr Ljunggren's experience with the instability of mercury in monitors irradiated in a reactor. We finally relied on the addition of sulphide ions to monitors spiked with mercury. We could not, however, measure the monitor mercury without doing chemistry. The sealed quartz vials are chilled with dry ice, cracked open and placed immediately in hydrochloric acid solution containing mercury carrier. Since Hg and  $\text{Hg}^+$  exchange very rapidly, no trouble with tracer loss or radiochemical equilibration should exist.

While speaking of equilibration I should like to point out the following. In preparing samples for analysis after irradiation, whether by acid dis-

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solution or fusion, the carrier should always be present at the time the sample is dissolved. In this way the carrier is always present in high concentration, which avoids loss of the desired tracer by absorption on walls or possibly even by volatilization.

A. H. W. ATEN (*Netherlands*): In our Institute we do not have a whole department for activation analysis, so you must not expect any complete descriptions of technical procedures from me. I can only give you some rather general remarks concerning the advantages and drawbacks of fast neutron activation.

A cyclotron produces quite a lot of neutrons, but they are formed with quite high energies and to make them thermal we have to use a lot of paraffin or other moderator, which means that the thermal flux obtainable is rather low.

It is therefore interesting to see what one can do with fast neutrons. Samples for fast neutron irradiation can be placed very near the target, and then the flux is several orders of magnitude higher.

I wish to make it clear that a cyclotron is by no means the ideal instrument for fast neutron activation analysis. With a cyclotron:

(1) It is almost impossible to irradiate several samples at the same time in identical positions.

(2) It is not easy to put several samples into exactly the same spot for a series of successive irradiations.

(3) It is often difficult to keep the beam current constant.

(4) The energy of the neutrons does not have a definite value, but varies over a large range. (The best neutron production is obtained by bombarding beryllium with deuterons.)

I have no experience with the  $(D + T)$  reaction, but I did work with an accelerator giving  $(D + Li)$  neutrons during the war. I have the impression that, in general, accelerator tubes will be more satisfactory for fast neutron activation analysis, unless one wishes to use a high flux. For activation analysis work with a machine factors come into play which are of no importance to people who use a reactor.

The most important point is that irradiation time with an accelerator is very expensive, so one tends to choose a nuclide with a short half-life, so as to reach or approach saturation as quickly as possible.

Also the individual cross-sections of the different nuclides do not vary nearly as much for fast neutrons as they do for slow neutrons, although the differences are still important enough to influence the choice of our reaction. Then one has to keep in mind that with fast neutrons quite a number of different types of reactions may occur with cross-sections that are not too different:  $(n,2n)$ ,  $(n,p)$ ,  $(n,\alpha)$  and—at least with a cyclotron—also  $(n,\gamma)$ .

Fast neutron activation is of particular interest for those elements among the rare earths with which slow neutron activation is not very successful, that is, for the lightest elements, lanthanum, cerium, praseodymium and neodymium.

The target material should be in the form of the oxide, which means that  $^{15}O$  will be produced by the  $^{16}O(n,2n)^{15}O$  reaction.  $^{15}O$  is a positron emitter with a half-life of 2 min. A correction is easily made as it is recognized by its half-life, and its intensity can be measured by a separate

irradiation of a compound which gives essentially pure  $^{15}\text{O}$  activity. For this purpose we irradiate lithium carbonate. Some  $^{11}\text{C}$  is produced by the  $^{12}\text{C}(\text{n},2\text{n})^{11}\text{C}$  reaction, but the amount is negligible if the irradiation time is comparable to the half-life of the oxygen.

To get the highest accuracy one would of course have to use an internal standard, but for approximate determinations such as for checking the purity of materials, one may integrate the beam current over the irradiation period and obtain quite reasonable results. If the beam current is not constant the irradiation time should be comparable to the half-life of the radioisotope produced.

Irradiation of praseodymium with fast neutrons produces an appreciable quantity of  $^{140}\text{Pr}$  by the  $^{141}\text{Pr}(\text{n},2\text{n})^{140}\text{Pr}$  reaction. This praseodymium isotope is a positron emitter and has a half-life of 3.4 min. A 200 mg sample

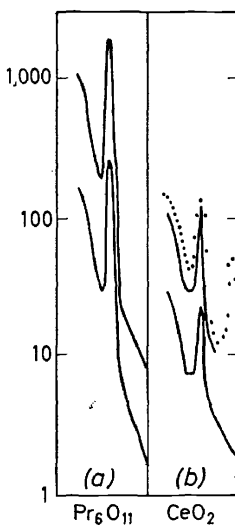


Figure 5. Spectra of irradiated praseodymium oxide (a) and cerium oxide (b)

of praseodymium oxide irradiated for 4 min in the Amsterdam cyclotron, and measured 3 min and 13 min after irradiation, gave the spectra shown in Figure 5(a). It can be seen that in ten minutes the activity has decayed by a factor slightly less than ten, which agrees with a half-life of 3.4 min. The amount of  $^{15}\text{O}$  produced is negligible, amounting to less than 1 per cent of the positron activity of praseodymium. However, this would not be the case if the praseodymium were an impurity present in small concentration in another rare earth oxide.

This reaction may be used for the detection of praseodymium in the oxides of other elements. Figure 5(b) shows the spectra obtained after irradiation of a sample of cerium oxide of unknown purity. The two spectra were measured 3 min and 13 min after the end of the irradiation. The latter spectrum shows the presence of the  $^{140}\text{Pr}$  quite clearly. The spectrum obtained 3 min after the end of the irradiation is shown as the

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dotted line in *Figure 5(b)*. To the right of the  $^{140}\text{Pr}$  annihilation peak there is interference from a 0.74 MeV gamma line due to  $^{139}\text{Ce}$  produced by the  $^{140}\text{Ce}(n,2n)^{139}\text{Ce}$  reaction. Since the  $^{139}\text{Ce}$  has a half-life of about 1 min this interference does not appear in the spectrum measured 13 min after the end of the irradiation. The spectrum obtained 3 min after irradiation shown by the full line in *Figure 5(b)* has been corrected by subtracting the spectrum obtained from an irradiated sample of very pure cerium oxide. The praseodymium content from both the three- and thirteen-minute spectra works out at about 6 per cent. This sample was of course a very crude cerium oxide and it would be quite possible to detect a much smaller amount of praseodymium.