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İSTANBUL - TURKEY

ÇNAEM-R- 178

APPLICATION OF THE IODINATED RESIN TO THE DETERMINATION OF THALLIUM IN BIOLOGICAL SAMPLES BY PAST NEUTRON ACTIVATION ANALYSIS

Sevim OKAR and Meriç ALKAN

P.K. 1, Hava Alanı, İstanbul, Turkey

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A B S T R A C T

A rapid, simple and highly specific method for determination of thallium in biological materials is described.

We have combined the fast neutron activation and separation technique by iodinated resin for thallium determinations. Irradiated samples were mineralized after appropriate decay periods. The digested samples were passed through an anion exchange resin previously treated with a saturated solution of I_2/KI. The iodinated resin presents specific retention also for Tl^{3+} together with Au^{3+}, Hg^{2+} and Ag^{+}. The resin containing these ions was directly counted with a multichannel gamma spectrometer. The yield of Tl^{3+} retention is over 98%.

In the presence of gold, silver and mercury, thallium contents of the biological samples can be determined by the proposed combined techniques by applying both appropriate irradiations and decay intervals for counting.

Ö Z E T

İYOTLANDIRILMIŞ REÇİNELERİN HIZLI NÖTRON AKTİVASYON ANALİZİ İLE BİYOLOJİK MADDELERDE TALYUM TAYİNİNDE KULLANILMASI

Biyolojik maddelerdeki talyum tayini için basit, hızlı ve oldukça spesifik bir yöntem verilmiştir.

Bu çalışmada, talyum tayinleri için hızlı nötron aktivasyon analizi ile iyotlandırılmış reçineler üzerinde ayırma tekniği birleştirilerek kullanılmıştır.

Işınlanan örnekler, uygun soğuma sürelerinden sonra asitte çözülmüş ve bu çözeltiler, doymuş bir I_2/KI çözeltisi ile muamele edilerek hazırlanmış anyon değiştirici reçine kolonundan geçirilmiştir. İyotlandırılmış reçinenin, Au^{3+}, Hg^{2+} ve Ag^{+} ile birlikte Tl^{3+}

iyonlarını da spesifik olarak tutma özelliği olduğu saptanmıştır. Bu tutulan iyonları taşıyan reçine, çok kanallı bir gamaspektrometresinde sayılmıştır. Tl^{3+} iyonlarının reçine üzerinde % 98'in üzerinde bir verimlilikle tutulduğu görülmüştür.

Hızlı nötron aktivasyon analizi ve iyotlandırılmış reçine üzerinde ayırma tekniğinin birleştirilmesi ile , ışınlama ve sayım için gereken soğuma süreleri ayarlanarak altın, cıva ve gümüşle birlikte olduğu zaman da biyolojik örneklerdeki talyum tayin edilebilmektedir.

C O N T E N T S

APPLICATION OF THE IODINATED RESIN TO THE DETERMINATION OF THALLIUM IN BIOLOGICAL SAMPLES BY FAST NEUTRON ACTIVATION ANALYSIS

Sevim Okar and Meriç Alkan

I. I N T R O D U C T I O N

Most of the rat poisons used today contain thallium and are involved in many accidental as well as intentive cases of human poisoning. Therefore, a specific determination method for thallium was of interest. Determination of trace amounts of thallium by neutron activation analysis generally depends on ^{204}Tl [1] and ^{206}Tl [2] isotopes. Since both of these isotopes are only beta emitters with either a very long or a very short half-life, excessively careful radiochemical purifications are necessary.

On the other hand, the possibility of using a specific neutron activation analysis method based on ^{202}Tl isotope produced by $^{203}Tl(n,2n)\,^{202}Tl$ reaction was investigated by M. T. Erben and S. Okar [3]. Although the gamma emitting property and convenient half-life of ^{202}Tl make the analysis specific, the necessary radiochemical purification steps are time consuming [4].

In this work we have searched the analytical methods in order to minimize the necessary radiochemical purification. For the separation of thallium we have based on a work performed by Heurtebise [5]. Heurtebise had shown that mercury, gold and silver ions, i.e. ions of elements which have the same chemical properties as the ions of thallium, could be separated by retention on iodinated or brominated anionic resins, from a number of other ions generally found in most analytical matrices. We have indeed

observed that when the solutions of irradiated hair samples were passed through the iodinated resin column, Tl^{3+} ions were also retained on the resin.

In the first part of this work the retention study of thallium on iodinated resin is presented. ^{202}Tl isotope was used as a tracer to study the retention of thallium on iodinated resin, and to investigate the effect of pH on retention, and also for the determination of resin capacity for thallium.

The second part of this work includes the application of the proposed method to toxicology. In the case of human poisoning, administered thallium is excreted mainly through kidneys and is accumulated in hair [6]. Therefore, hair samples spiked with thallium and a urine sample from a patient were used for the toxicological studies.

We have combined the fast neutron activation and separation techniques in order to achieve to a specific and more rapid determination method for thallium.

II. E X P E R I M E N T S

Preparation of iodinated resin column: 200 mg of strongly basic anion exchange resin, Dowex 2x10 (200-400 mesh, Cl^- form) was placed in a glass column of 5 mm diameter. The resin was iodinated by passing 15 ml iodine-iodide solution through the column according to Heurtebise. Iodine-iodide solution contains 25 gr of iodine in 1 liter of 1 M KI solution. After washing the iodinated resin in the column with a few milliliters of water, the column was ready for use.

These columns were used in order to investigate the retention of thallium, the effect of pH on retention, and the resin capacity for thallium.

Experiments were run with hair samples for the radiochemical separation studies of thallium in biological specimens. Besides, preliminary experiments were carried out with a dry-ashed urine sample which was obtained from a patient subjected to thallium poisoning.

Determination of thallium in hair: 250 mg hair samples spiked with thallium were sealed in quartz ampoules. Known amounts of metallic thallium, gold and silver sealed in quartz ampoules were used as standards. Hair samples and standards were irradiated for two different durations as follows:

a. Short irradiation with thermal neutrons for only gold determination: Hair samples and a gold standard were irradiated for two hours in TR-1 reactor at a thermal neutron flux of about 1.2×10^{12} $n.cm^{-2}.sec^{-1}$. After a decay period of 2-3 days, the quartz ampoules were broken, hair samples were dissolved in conc. HNO_3 and then pH of the solution was adjusted to 2.5. The solutions were allowed to pass through the resin column by their own weights.

   After passing the hair solution through the resin column and washing the resin with 5 ml of 10% NaBr solution followed by 20 ml of water, the resin was transfered to a glass counting disk of 25 mm diameter, and dried.

   The gold standard was dissolved in aqua regia, a proper aliquot of the gold solution was pipetted into a beaker and the pH of the solution was adjusted to 2.5. The standard gold solution was passed through and identical resin column and the resin was prepared for counting as the same manner of hair samples.

b. Long irradiation with fast neutrons for thallium determination: Hair samples together with thallium, gold and silver standards all sealed in separate identical quartz ampoules were irradiated for 30 hours (cumulative) in TR-1 reactor in the vicinity of the fuel element where the fast neutron flux was higher. The samples and the standards were processed as described above and counted after appropriate decay periods.

   A 400 channel gamma spectrometer equipped with a 3in.x 3in. NaI(Tl) crystal was used for radioactivity measurements.

III. RESULTS AND DISCUSSION

The retention of thallium on iodinated resin is over 98 percent. The maximum amount of thallium retained on 200 mg of resin is found to be 650 µg. There is no effect of pH of the solution on retention of thallium between pH 1 and 8. But very acidic or basic solutions cause decomposition or deterioration or iodinated resin [5]. Our experiments were performed at pH 2.5 in order to avoid the retention of iron ions on resin.

The gamma-ray spectrum of iodinated resin after passage of hair irradiated with fast neutrons is given in Figure 1.

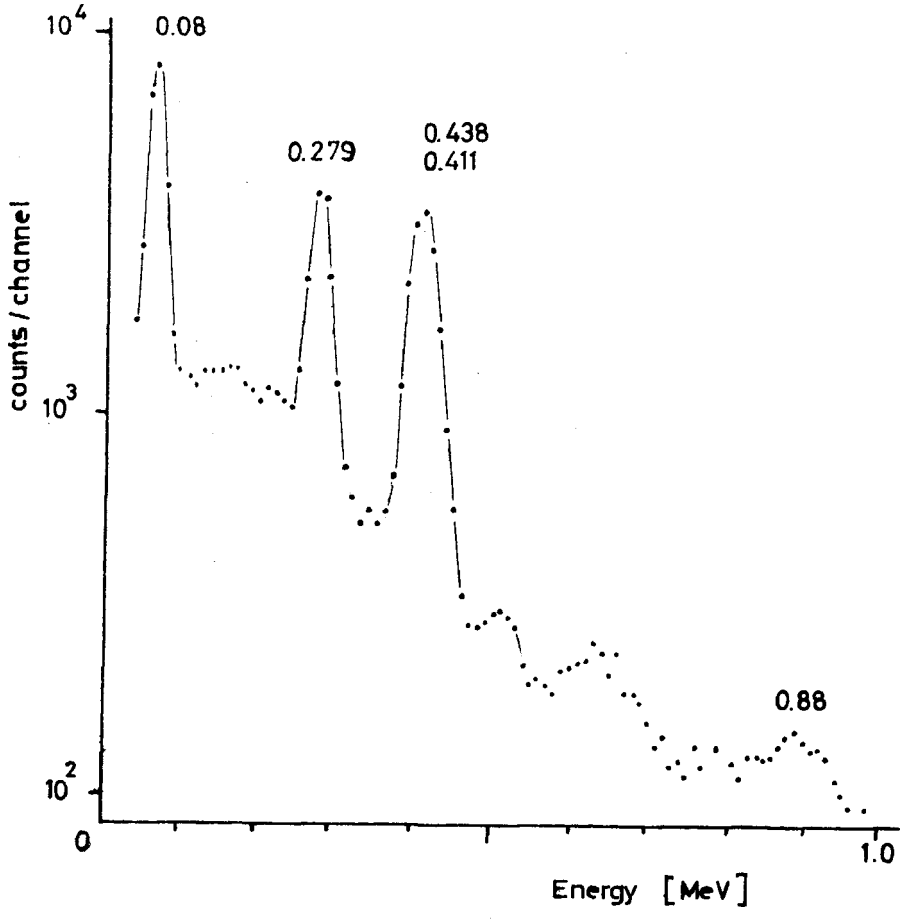

Figure 1. Gamma-ray spectrum of iodinated resin after passage of hair sample irradiated with fast neutrons

In this spectrum, X-ray peak around 0.08 MeV is a combined peak of all isotopes of ^{204}Tl, ^{202}Tl, ^{197}Hg, and ^{198}Au [7]. The peak at 0.279 MeV region which belongs to the ^{203}Hg, does not interfer in thallium determination. Thallium content of the hair could be calculated by measuring the 0.438 MeV activity of ^{202}Tl. But 0.411 MeV gamma peak of ^{198}Au is overlapped with this peak of ^{202}Tl. The difficulty in the calculation of the amount of thallium because of the presence of the gold peak in the same area was overcomed by performing a short and a long irradiation at a thermal and a fast neutron flux respectively. In this way, through the short irradiation with thermal neutrons, ^{202}Tl isotope can not be produced. This leads to the possibility of determining of tha amount of gold. The gold content of hair determined in this way is 0.04 $\mu g/g$. In the case of long irradiation with fast neutrons, it was necessary to strip the component of ^{198}Au from 0.438 MeV photopeak area of ^{202}Tl prior to the calculation of thallium.

If the sample contains also considerable amount of silver,as in our hair sample, one can first determine the amount of silver through 0.88 MeV peak of ^{110m}Ag activity. Thus, its contribution to the peak of interest at 0.438 MeV, can be resolved. Silver content of our hair sample analyzed is found as 0.02 $\mu g/g$.

IV. C O N C L U S I O N

Determination of thallium in hair and urine samples by the combined method of fast neutron activation and separation of thallium by iodinated resin is suitable when the amount of thallium present in the sample is over 1 μg.

When the analytical result is not urgently needed only long irradiation is carried out, the sample is cooled for complete decay of gold (about 25 days), and then silver contribution is taken into consideration for thallium calculation.

But when the analytical result is rather urgently needed, the amount of gold in hair is determined in a separate sample by means of a short irradiation, and its contribution to 0.438 MeV peak is considered together with that of silver without waiting for the decay of gold in long irradiated samples. This way of determination should also be applied when the amount of thallium is about in the limit of sensitivity.

It is finally worth to mention that our previous experiments with urine samples have proved that urine is a better basis for detection thallium poisoning. Especially, when the samples are taken at the beginning of poisoning, since the excretion of thallium through kidneys is about 15.4% in 5.5 days.

On other hand, hair samples preferably are used for the detection of thallium poisoning which may have occured some time ago since the highest concentration of thallium which remains in the body is in the hair.

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