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QUICK METHODS FOR RADIOCHEMICAL ANALYSIS

FOREWORD

Quick methods for radiochemical analysis, of adequate precision for the assay of a limited number of biologically important radionuclides, are important in the development of effective monitoring programs, particularly those that would be applied in emergency situations following an accidental release of radioactive substances.

Methods of this type have been developed in a number of laboratories and are being altered and improved from time to time. They are often not published in the open literature even though they could be of considerable interest to other laboratories and institutes. Several rapid methods are given in a report prepared jointly by the World Health Organization, the Food and Agriculture Organization of the United Nations and the International Atomic Energy Agency. This report was published under the title "Methods of Radiochemical Analysis" by WHO in Geneva, in 1966.

A panel of experts which met in Budapest in 1966 to advise the Agency on the co-ordination of research in radiation protection recommended that particular attention be given to these rapid radiochemical techniques. The Agency thereupon invited several Member States to provide detailed information on any such procedures that might have been developed in their laboratories. From the information thus obtained a number of methods have been selected that appear to meet the criteria of speed and economy in the use of materials and equipment, and seem to be eminently suitable for those radionuclides that might be of major interest from the point of view of assessing the potential dose to persons following a serious dispersal of contamination.

The material provided has been edited with the aim of achieving a more uniform presentation. It is hoped that the booklet will prove to be of general interest, and Member States are invited to send to the Agency any additional material or modified procedures that they would wish to be considered for inclusion in future revised editions.

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The method is based on the coprecipitation of caesium with Prussian blue. Since the number of operations is small, the procedure makes it possible to achieve a high degree of yield and high radiochemical purity.

PROCEDURE

An amount of 5-10 mg of caesium carrier and 1.6 ml of 0.5M $FeCl_3$ is added to 1 litre of water, acidified with several millilitres of conc. HCl or HNO_3. The solution is stirred vigorously with a stirrer and Prussian blue is precipitated with approx. 1.5 ml of 0.5M $Na_4Fe(CN)_6$. The total volume of the precipitating agent is added in drops within about 1 min. After 1-2 min of stirring the precipitate is allowed to sediment. The clear solution above the precipitate is filtered using a fine filter paper and the remainder is separated by centrifuging. The precipitate is washed by means of decantation with small portions of distilled water till the reaction of the washing liquid is neutral. The precipitate, including the small amount on the filter paper, is completely dissolved in 16 ml of saturated EDTA solution (pH10) and the mixture is then placed on a boiling water bath. The brown-red solution is diluted by adding an equal volume of water, and Prussian blue is re-precipitated by adding conc. HCl until pH0-pH1.

Specimens obtained by coprecipitating caesium-137 with Prussian blue are suitable for gamma spectrometric determinations even without purifying the precipitate by means of re-precipitation. For the determination of the beta activity of the specimens the following refining procedure is necessary:

After dissolving the Prussian blue precipitate several times in alkaline EDTA solution (pH10) two alternative procedures may be followed:

(a) Caesium is extracted twice, using each time 3 ml of 0.1M sodium dipicrylaminate in nitrobenzene; 5 min of extraction are sufficient. After washing the organic phase with strongly diluted EDTA solution, caesium is re-extracted three times, using each time 1 ml of 1M HNO_3. After evaporation of the solution to dryness on a measuring plate, specimens with very low mass-per-unit area are obtained.

(b) Caesium tetraphenyl borate is precipitated from the hot solution with approx. tenfold excess of sodium tetraphenyl borate, the precipitate is separated by centrifuging or filtration and washed with 1% acetic acid solution.

Additional information to this method may be found in the literature quoted below.

REMARKS

The analysis together with the final gamma spectrometric measurement takes about 60 min. The beta activity measurement takes about 30 min more.

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DETERMINATION OF CAESIUM-137 IN LIQUID MILK

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A technique for determining caesium-137 in milk on the basis of caesium-137 sorption has been adapted according to the method of Broadbank. The caesium carrier is not added, because its addition decreases the sensitivity of measurement.

Two procedures were used for the assay of caesium-137 in milk:

(a) Sorption of caesium-137 from the solution of milk ash dissolved in 3M HNO_3
(b) Sorption of caesium-137 from whey.

In both methods the radioactivity of caesium-137 was determined directly on the ammonium molybdophosphate (AMP) bed by means of counting.

PROCEDURE

1. Preparation of ash solution

The milk is evaporated and ashed below 450°C to avoid loss of caesium. 10 g of milk ash is damped with 10 ml of distilled water and then dissolved in 60 ml 0.5N HNO_3 (prepared from HNO_3, sp.gr. 1.4).

The ash solution is filtered through paper pulp into a graduated cylinder. Water is added to adjust the volume of the solution to 150 ml.

2. Preparation of whey from liquid milk

250 ml of milk is poured into a 400 ml beaker. At the same time 25 ml of diluted CCl_3COOH (100 g of CCl_3COOH + 50 ml of H_2O) is added and the sample is mixed well. After about 10 min 50 ml of HNO_3 (sp. gr. 1.4) is added and the sample is stirred and left for 30 min. The mixture is filtered using vacuum through a bed of filter pulp on a Büchner funnel and washed with a small amount of water. The solution is placed in a 500 ml graduated cylinder, 40 ml of conc. HNO_3 (sp. gr. 1.4) is added and the volume of the solution is adjusted to 500 ml with water.

3. Preparation of a bed of ammonium molybdophosphate (AMP)

7 ml of NH_4NO_3 solution (71.4 g of NH_4NO_3 in 134 ml of HNO_3 of sp. gr. 1.4, diluted to 1000 ml with distilled water), 3 ml of 10% solution of $(NH_4)_6Mo_7O_{24}.H_2O$, and 1 ml of $NH_4H_2PO_4$ (3.62 g of $NH_4H_2PO_4$ in 500 ml of H_2O) are mixed in a 50 ml beaker, heated at 80°C for 20 min and then cooled to room temperature. The yellow precipitate of AMP (120 mg) is collected in a radiochemical funnel on a bed of paper pulp and washed with distilled water to remove the acid. The diameter of funnel surface should

fit the surface of the window of a GM counter (about 2.0 cm in diam.). The AMP bed should cover the surface of the filter.

4. Sorption of caesium-137 on the AMP bed and counting

The solution of ash or whey is filtered under reduced pressure through the prepared bed for at least 20 min. The filter is then taken out together with the bed of AMP, placed on a dish and counted, using an end-window GM counter with a mica window of 1.5 mg/cm^2 thickness.

The standard preparation of caesium-137 is also made on a bed of AMP. For this purpose a standard solution of ^{137}CsCl of a known activity is prepared in 3M HNO_3. The solution is filtered through a bed of AMP. The conditions for sorption of caesium-137 on the AMP bed are to be identical with those applied to the unknown solutions examined.

The specific activity of milk is expressed in pCi/litre. It is calculated from the following formulae:

Sorption of caesium-137 from the solution of ash:

$$a_m = \frac{N_p a_w X 100}{N_w b Y}$$

Sorption of caesium-137 from whey:

$$a_m = \frac{N_p a_w 400}{N_w Y}$$

where
N_p = counting rate for the sample (counts/min)
N_w = counting rate for the standard solution (counts/min)
a_w = activity of the standard solution (in pCi)
b = weight of ash
X = content of ash (g/litre)
Y = recovery of caesium-137 (in %).

REMARKS

This method permits the determination of caesium-137 activity greater than 200 pCi in 1 litre of milk. Recovery of caesium-137, as determined by this method, is 75.9 ± 7.8%. The determination of caesium-137 can be completed in 3 h.

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RAPID METHOD FOR DETERMINATION OF CAESIUM-137 IN WATER AND URINE

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The method is selective in the presence of several nuclides and enables us to determine 2.2×10^{-5} μCi and 5.1×10^{-5} μCi of caesium-137 per millilitre of water or urine samples respectively; it is especially convenient for routine measurements of personnel contaminations.

The method is based on ion exchange of caesium-137 on ammonium molybdophosphate (AMP) mats. A modification of the method permits the detection of caesium-137 in water in amounts of approximately 1 pCi. The modification consists in changing the size of AMP mats and omitting the asbestos. This enables the measurements of the samples to be carried out in a low-background counting unit.

PROCEDURE

Prepare the following working solutions:

(a) NH_4NO_3 solution: dissolve 71.4 g of NH_4NO_3 in 95.6 ml of conc. HNO_3 (sp. gr. 1.5) and adjust with H_2O to 1000 ml.

(b) $NH_4H_2PO_4$ solution: dissolve 3.62 g of $NH_4H_2PO_4$ in 500 ml H_2O.

(c) Ammonium molybdate solution: dissolve 26.5 g of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in 250 ml H_2O.

Add to a 250 ml beaker 90.3 ml of NH_4NO_3 solution and 38.7 ml of ammonium molybdate solution. Stir well and heat for 17 min in a water bath at 80°C. Add 0.5 g of Gooch asbestos and 12.9 ml of $NH_4H_2PO_4$ solution. Stir and heat at 80°C for 10 min. Then cool to room temperature. This mixture should be freshly prepared before analysis.

Place a soft filter paper on the 9 cm diameter sintered filter funnel 25G2, stir the above mixture well and pour it into the funnel. Wash the beaker with 20 ml of water and add the washings to the funnel. Suck off most of the liquid using vacuum.

Place a hard filter paper on the yellow surface of asbestos with AMP and suck through 50 ml of water. The suction should be strong enough to avoid the separation of layers of the mat. Stop the suction and pour on the mat the water or urine sample prepared as follows:

(a) Urine sample: to 1000 ml of urine add 100 ml of conc. HNO_3

(b) Water sample: acidify 1 litre of water sample with 100 ml of conc. HNO_3 and add 250 mg of NaI.

Drain the sample through the AMP mat and control the suction so as to obtain a flow rate of about 50 ml/min. After draining off most of the sample, wash the mat with 200 ml of diluted HNO_3 (1 + 10). Discard the top filter paper (which should not be coloured by the yellow part of the

mat). Strip the mat from the filter funnel and wrap it around a glass GM counter.

Calculate the results, using blank AMP mat counts per minute as a background.

PROCEDURE FOR A MODIFIED METHOD

The working solutions are prepared in the same way. Add to the 50 ml beaker 7 ml of NH_4NO_3 solution and 3 ml of ammonium molybdate solution. Stir well and heat for 15 min in a water bath at 80°C. Add 1 ml of $NH_4H_2PO_4$ solution, stir and heat at 80°C for 10 min. Then cool to room temperature. This mixture should be prepared freshly as required. Place a hard filter paper on a 25 G2 sintered disc and mount it in a demountable filtration funnel. Stir the mixture well and pour it into the funnel. Wash the beaker with 5 ml of water and add the washings to the funnel. Suck off most of the liquid using vacuum.

On an AMP mat prepared in this way pour rainwater which is acidified with 100 ml of conc. HNO_3 per 1000 ml of water and in which 250 mg of NaI per 1000 ml is dissolved. The volume of the demountable filter funnel is usually much smaller than that of the sample. When adding new portions of the sample, special care should be taken to prevent disturbing the mat surface. After sucking off the last portion of the sample, wash the filter funnel with 10 ml of 96% ethanol. Suck off the mat to dryness and transfer it to the bottom of an inverted beaker. Then cover the mat with collodion film prepared as follows: Mix 50 vol.% of collodion with 25% of amylacetate and 25% of ether and store the mixture in a tightly closed bottle. Drop one drop of the mixture upon the surface of the distilled water in a 300 ml crystallizer. When the collodion film begins to contract, take it out of the water with a wire ring of 4 cm in diam. so that the upper surface of the film remains dry. Such a film is approximately 30 $\mu g/cm^2$ thick. Cover the AMP mat with the dry surface of the film and fold the edges of the film below the paper base of the AMP mat.

Transfer the mat to a circular piece of scotch tape, 2.6 cm in diam., and cover it with a paper ring so that the AMP mat is fully exposed and the edge of the collodion film and scotch tape are completely covered.

Place the AMP mat on the plastic disc (1.8 cm in diam.) of the low-background beta counting unit and measure the beta activity of the sample.

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DETERMINATION OF IODINE-131

RADIOMETRIC DETERMINATION OF IODINE-131 IN WASTE WATERS

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The iodine is extracted by chloroform and this extract is gamma counted if the activity is higher than $10^{-4}\mu Ci/ml$. If the activity is lower, the iodine is re-extracted and the AgI is precipitated and beta counted. The yield of enrichment and separation is determined by spectrophotometry.

PROCEDURE

An amount of 1-10 ml of the sample is placed in a 60 ml separating funnel and the solution is neutralized (using indicator paper) with 4N HNO_3 or 4N NaOH solution. Then 10 ml of 2M Na_2CO_3 solution is added, 0.2 ml of standard solution (13 g NaI per 1 litre of water containing 4-5 mg $NaHCO_3$) if the activity is higher than 1×10^{-4} $\mu Ci/ml$, or 2 ml if the activity is lower, and 1 ml of NaClO solution (5% of chlorine). The mixture is shaken for 5 min and 5 ml of conc. HNO_3 is added dropwise. After the reduction of iodate with 9 ml hydroxylamine hydrochloride solution (70 g/litre) the iodine is extracted with 10 ml of chloroform and the aqueous phase is rejected. 10 ml of water is added to the separating funnel containing iodine in $CHCl_3$ solution and a few drops of $NaHSO_3$ solution (104 g/litre) until the $CHCl_3$ layer is colourless. It is then rejected.

(a) The activity of the sample is believed to be higher than 1×10^{-4} $\mu Ci/ml$

1 ml of 6N HNO_3, 4-5 drops of $NaNO_2$ solution (69 g/litre) and 10 ml of $CHCl_3$ are added in turn to the aqueous iodide solution in the separating funnel. After shaking the $CHCl_3$ layer is transferred to a 20 ml volumetric flask. The funnel is washed with 5 ml of $CHCl_3$ which is transferred to the volumetric flask. The volume is then filled up to the mark with $CHCl_3$.

An aliquot of the $CHCl_3$ solution is then gamma counted using a comparative sample with known content of iodine-131.

The recovery of iodine is checked chemically. The comparative solution is prepared as follows: 0.2 ml of standard solution is placed in the 60 ml separating funnel and 1 ml of 6N HNO_3, 10 ml of water and 4-5 drops of $NaNO_2$ solution (69 g/litre) are added. The iodine is extracted three times, each time using 5 ml of $CHCl_3$, and the organic phases are collected in a 20 ml volumetric flask. After filling up to the mark the absorbancy of the comparative solution and that of the sample solution are measured at 510 nm in a cuvette of 1 cm path length. The ratio of absorbancy gives the recovery factor.

(b) The activity of the sample is believed to be lower than 1×10^{-1} μCi/ml

1 ml of 6N HNO_3 is added to the aqueous solution of iodide and the mixture is heated nearly to boiling. Then 2 ml of 0.1N $AgNO_3$ solution is added and the precipitate is filtered through the filter paper on a special demountable type of Büchner funnel. The precipitate is washed three times with 5 ml of water, three times with alcohol, dried at 110°C, beta counted, using a comparative source of known iodine-131 content, and finally weighed.

The chemical recovery is calculated from the ratio of the mass obtained by weighing the AgI recovered from the sample with the theoretical value (37 mg) corresponding to the added volume of standard solution of NaI.

REMARKS

The method is applicable to the following iodine concentrations:
In case (a) – higher than 1×10^{-4} μCi/ml;
In case (b) – ranging from 2×10^{-6} μCi/ml to 10^{-4} μCi/ml.
The time necessary to perform two parallel determinations is about 30 min.

DETERMINATION OF IODINE-131 IN MILK

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PROCEDURE

Improved method of dry-ashing of milk

The simple ignition of the sample at high temperature results in a loss of iodine through evaporation. To minimize the iodine loss, a NaOH solution is added to the milk prior to ignition. It is recommended to add a 1N NaOH solution to the milk in the ratio of 1:19.

Determination of organic and inorganic iodine in milk

According to the method reported by Bergh [2nd Int. Conf. peaceful Uses atom. Energy (Proc. Conf. Geneva, 1958) 18, UN, New York (1958) 508], organic and inorganic iodine are determined separately. However, it is confirmed by our experiment that the inorganic iodine, obtained by oxidizing iodide-ions with $NaNO_2$, combines with casein and fat during the later chemical treatment according to Bergh's method. To determine the individual forms of iodine in milk, it is recommended to adopt the ordinary separation method of fat and protein, such as ether extraction of fat and trichloroacetic acid (TCA) precipitation of protein.

Determination of inorganic iodine

To determine inorganic iodine in fresh milk, a composite system of ion exchange and CCl_4 extraction is recommended. An amount of 3-5 ml of Dowex 1X8 resin (20-50 mesh, NO_3^- form) is charged in a column of 1 cm diam. and 30 cm length. 200 ml of fresh milk containing 10 mg of iodine carrier (NaI form) is passed through it. After washing the resin with warm water, the iodine is eluted with 400-500 ml of 2N $NaNO_3$ (or 200 ml of 4N $NaNO_3$). 100 ml of CCl_4, 1-2 g of $NaNO_2$, and 5 ml of HNO_3 are added to the eluate and shaken vigorously in the separating funnel. The iodine, extracted to CCl_4 layer, is transferred to water layer by shaking with water containing a few drops of SO_2 solution. After the volatilization of SO_2 by heating, AgI is precipitated by adding $AgNO_3$ solution, filtered (or centrifuged) and counted.

A milk sample deteriorated during a long period of transport is hard to pass through an ion-exchange resin column because of its pasty condition. Therefore, a method with TCA treatment and CCl_4 extraction can be recommended. To 200 ml of deteriorated milk 90 ml of 30% TCA solution is added and the mixture is centrifuged. 50 ml of CCl_4 and 2 g of $NaNO_3$ are added to the supernatant and the subsequent treatment of the mixture is the same as that outlined above.