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EUROPEAN ATOMIC ENERGY COMMUNITY - EURATOM

SOME CHEMICAL PROCEDURES
FOR THE RADIOLOGICAL MONITORING
OF THE ENVIRONMENT

by

M. de BORTOLI (EURATOM, JRC - Ispra)
and
E. VAN DER STRICHT (European Communities - Luxemburg)

1969

Joint Nuclear Research Center
Ispra Establishment – Italy
Protection Service

and

Directorate General Health and Safety
Luxemburg

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Joint Nuclear Research Center - Ispra Establishment (Italy)
Protection Service and
Directorate General Health and Safety - Luxemburg
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Particularly, procedures are given for the separation of strontium, caesium
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ABSTRACT

This report describes some chemical methods used at the Protection Service by the group which is charged with the survey of environmental radioactivity on the site of the Euratom Ispra Establishment.

Particularly, procedures are given for the separation of strontium, caesium and plutonium and for the determination of uranium in some materials like water, atmospheric dust, soil and others in the food chains.

KEYWORDS

ENVIRONMENT
RADIOACTIVITY
MEASUREMENT
DETERMINATION
CAESIUM
STRONTIUM

PLUTONIUM
AIR
WATER
SOILS
RADIOCHEMISTRY

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INTRODUCTION

This paper reports the principal techniques used, for the survey of radioactivity on the site of the Euratom Ispra Establishment, at the chemical laboratory of the Protection Service.

As the text is conceived to fulfil different requirements, like requests from outside the laboratory, training of the personnel, of stagers and students, etc., to the expert it may appear unnecessarily prolix and rich in obvious details, particularly in the sections dealing with the collection and preparation of the samples.

These persons are kindly asked to pass over the parts they will judge superfluous and to consider only those which look interesting.

The characteristics of the reagents have been given whenever necessary. The concentrated (conc.) acids and alkalis used are commercially available and have the following concentrations

Hydrochloric acid	HCl	32 - 36	%
Hydrofluoric acid	HF	38	%
Nitric acid	HNO_3	65	%
Perchloric acid	$HClO_4$	70	%
Phosphoric acid	H_3PO_4	85	%
Acetic acid	CH_3COOH	99	%
Ammonium hydroxide	NH_4OH	25	%

The diluted acids and alkalis have been obtained by those mentioned above through addition of water in the given proportion.

1 - SAMPLING

1.1. <u>Introduction</u>   This is not the place to discuss fully the require-
ments that samples taken for environmental monitoring must satisfy.

This has already been a matter of debate on numerous occa-
sions even at international level (1, 2). Suffice it to say that the way
samples are collected is at least as important as the ensuing analytical
procedure : it is clear that to process nearly or totally unrepresentati-
ve samples amounts to a waste of time and money because the results
obtained cannot be used when they are to be interpreted.

Apart from the representativity of the sample it should be
kept in mind that unnecessarily big samples may cause great analyti-
cal difficulties due to matrix effects. It is therefore advisable to
consider the amount of sample needed to achieve the goals of environ-
mental monitoring programs. In certain cases it will suffice to state
that the radioactivity of the sample is below a preselected value ; the
sample need then only be sufficient in quantity to provide a reading
that shows reliably whether the activity is below the pre-established
level. If necessary, simplified chemical procedures with rough separa-
tions can then be adopted. The methods described below consider the
cases in which the data have to satisfy more stringent criteria of ac-
curacy and precision because the object is to acquire a better under-
standing of the radiological situation around a nuclear site, through
the study of the correlations existing between the data obtained from
different materials.

(1)   "Manual on environmental monitoring in normal operations",
      IAEA   Safety series, No. 16, 1966

(2)   "Guide pratique pour l'organisation de la surveillance de la
      contamination radioactive des denrés alimentaires et des
      boissons"
      Commission des Communautés européennes - EURATOM,
      décembre 1967.

As to the actual sampling, we limit ourselves to a brief re-wiew of the criteria to be observed when collecting samples, as regards both method and sampling devices.

1.2. Water Except in the case of very small pools or water courses, it is advisable to take the sample at a sufficient distance from bank and bottom to preclude as far as possible the presence in the sample of sus-pended materials such as mud, clay or fine sand.

If the collected water has to be stored for some time before treatment, it is advisable to add a preserving agent, such as nitric acid or perhydrol, to prevent the growth of algae and moulds.

1.3. Atmospheric dust This type of sample can be collected by dra-wing air into an electrostatic precipitator or cascade impactor or by drawing it through a filtering medium ; the latter is by far the most common method. The efficiency of collection depends on a great num-ber of factors. Good filtering devices should have high efficiency over the complete range of the particle spectrum, cause small pressure drop and maintain a fairly constant airflow over the complete period of sam-pling, regardless of dustload. This requirement is of special importan-ce when the volume of air passed through the filter is estimated by flow meter readings rather than with integration counters.

To lessen to a certain extent the influence of hot particles it is advisable to filter at least 300 m^3 per 24 hr period.

With a number of filters the efficiency changes with the dust loading and this effect should be taken into account where relevant. A number of filter papers or membranes are available which ensure near-ly 100 % efficiency for the atmospheric radioactive dust particles.

1.4. <u>Fall-out</u>   Fall-out may be wet (rain, snow, dew) or dry (dust). In the wet precipitation we may further distinguish between soluble and insoluble activity. Generally fall-out collectors are of the type which yields "total" (dry and wet) samples but there are others which collect dry and wet fall-out separately.

Basically, total fall-out is collected in two ways :

- first, exposing a vessel to accumulate precipitation ; at the end of the sampling period the rainwater is recovered from it, usually to be evaporated ;

- second, by using an ion exchange collector (see Fig. 1). The rainwater, collected in an appropriate vessel, first passes through a filter which retains the insoluble materials and then runs through cation and anion exchange columns. At the end of the collection period the sample is immediately ready for further treatment. To minimize losses during periods of drought the bottom of the collecting vessels should be covered with demineralized water. At the end of each sampling period the vessels must be carefully washed to ensure complete recovery and to avoid contamination of the next samples.

For further details on this topic see (1).

1.5. <u>Total human diet</u>   The most practical way of collecting these samples is to use the same vessel in which they will later be dried. This obviates any difficulty of transfering the fatty substances. This method is applicable only when the sample is taken in places close to the laboratory where they are to be treated. Where this is not the case, the transfer of the wet material is unavoidable.

---

(1)   "L'impiego delle resine a scambio ionico per il prelievo delle ricadute radioattive e la determinazione della frazione disciolta dei radionuclidi"   M.C. de Bortoli, P. Gaglione
Paper to be presented to the XIV Annual Meeting of the AIFSPR, Formia   29 - 31 May 1968.

1.6. <u>Herbage</u>   It is important to cut the grass stems at their base rather than to pull them up, in order to avoid an admixture of soil which might substantially change the concentration of both radioactivity and stable elements in the sample.

1.7. <u>S o i l</u>   The place chosen for sampling should, if possible, be fairly level, remote from buildings or high trees, well covered with grass, uncultivated, and not liable to be flooded, e.g. through flooding of a stream or lake.

When one is interested in the total activity or in the activity profile the most practical way of sampling is to take soil cores by means of (see Fig. 2) a steel cylinder of suitable diameter (e.g. 10 cm), sharpened at the lower edge to penetrate easily into the ground when hammered. Samples are taken at the desired depth by inserting a metal rod at right angles to the cylinder axis, through one of the couple of holes bored along the sides of the cylinder.

To ensure that samples are representative, each should consist of about ten cores taken roughly chequerwise over an area of 20 - 50 sq.m.

When the soil samples are taken with the aim of studying the movement of radioactivity between soil and grass, additional precautions should be taken to ensure a proper separation of the various parts of the samples.

2 - SAMPLE PREPARATION

2.1. <u>Introduction</u> Normally not all the samples collected are submitted to chemical separations, but also those which undergo direct radioactivity measurements only need some pre-treatment, in order to concentrate the radionuclides and to homogenize the sample. These aims are achieved mainly through the operations of dehydration, grinding and ashing.

2.2. <u>Dehydration</u> This process, which consists in removing water from the samples, is used for direct gamma spectrometry measurements on samples of insufficiently high specific activity. Drying is also a necessary pre-treatment step before ashing, whenever a chemical separation has to be effected.

   If no measurements are to be performed on the dried samples, it is advisable to dry them in the same vessels in which the samples are subsequently to be ashed, so as to avoid unnecessary transfer operations. Besides the normal laboratory materials, large pyrex glass trays of the ordinary household type have proved to be very suitable.

   Drying should be carried out at relatively low temperature if volatile radionuclides such as iodine isotopes, are present.

2.3. <u>Grinding</u> This operation is suitable whenever radioactivity measurements (gamma spectrometry) are to be effected on the dried substance.

   Soil samples are not to be ground, but simply homogenized after drying (since they are composed of several sub-samples) and sieved (normally through a sieve with 0.7 mm openings).

2.4. <u>Ashing</u> The object of this operation is to obtain, by removing the organic matter, a residue of ash or salts which can be dissolved and

thus chemically treated.

The regulation of the ashing temperature is extremely important whenever relatively volatile radionuclides, such as cesium-137, are to be determined. With this element, the temperature should not exceed 450°C, although probably there are no appreciable losses through volatilization up to 550° and perhaps even 600°C. Nevertheless, as certain materials herbage in particular, tend during ashing to develop heat, thus approaching the conditions of violent combustion (the mere opening of the furnace door may cause in such cases the firing of the sample), it is best to raise the temperature stepwise, with an intermediate stage of a few hours at 250°C. As to the duration of ashing generally speaking 15 to 24 hours should be sufficient, at the recommended temperature of 450°C. With samples that are richer in organic substances (milk, fish) it may prove effective starting the ashing in a domestic gas or electric oven, making sure first that it will not let the samples heat above 300°C. Another advantage of this preheating is that it obviates the formation of crusts and tar on the calcinating furnace itself.

If it is desired to speed up the calcination, or if the oxidation is exceptionally difficult, the ashes may be moistened, once or more often, with concentrated nitric acid, after the sample and its vessel have been taken out of the furnace and allowed to cool.

After ashing the carbon residue should be insignificant, which means that the ashes should be white and the residue on the filter after acid dissolution should be of a pale colour. The scope here is to avoid losses, in the carbon residue, of the elements and/or radionuclides analysed, losses which cannot be taken into account when correcting for the chemical recovery.

3 - SEPARATION OF STRONTIUM

The quantity to be submitted to the chemical processing varies with the different materials depending on their level of contamination and the degree of sensitivity aimed at. The chemical procedures described below refer, unless otherwise stated, to the following quantities of material :

A)   Atmospheric dust :   5 to 20 thousand m^3 of air filtered on a filter area of a few hundred to a few thousand cm^2.
Dry residue of atmospheric precipitations :   up to 5 grammes ;

B)   Fresh water :   50 - 200 litres ;

C)   Milk : 2 litres ;   Fish :   500 grammes (fresh weight) ;

D)   Grass and plants :   50 grammes (dry weight) ;

E)   Bones :   10 grammes (ash weight) ;

F)   Soil :   100 grammes (dry weight).

These quantities determined the amounts of the various reagents, the times, certain operations, etc. used in the chemical procedure. They are, however, valid as orders of magnitude in that significant difficulties should not be found in processing twice or half the quantities indicated.

3.1. Atmospheric dust on filters ; dry residue of atmospheric precipitations (fall-out)

1. Transfer the ashes into a PTFE (polytetrafluoroethylene) capsule, add 90 mg of strontium-carrier, 20 - 30 ml of conc. HF and 2 ml of conc. $HClO_4$. Evaporate to dryness on a sand bath.

2. Add to the residue, which should be very small (if not repeat the evaporation with HF), about 4 - 5 times its weight of a flux, consisting of NaOH and KOH 1:1 finely ground, and melt in the same vessel on a sand bath (the mixture melts at approximately 170°C).

3. After complete fusion, allow to cool, then dissolve the cake with water and HCl : normally there will be no residue.

4. Transfer the solution into a centrifuge tube and add NH_4OH until a pH of 9.5 is read at the pH-meter. Centrifuge and put the solution aside.

5. Dissolve the residue with the minimum amount of HCl, dilute and reprecipitate the hydroxides as in the preceding step.

6. Centrifuge and discard the residue, which can be used for the separation of Pu. Add the solution to that obtained in step 4., add 10 ml of a saturated solution of Na_2CO_3 and heat almost to boiling.

7. Allow to cool, make sure the precipitation is complete and centrifuge : discard the solution which can be used for the separation of cesium.

8. See paragraph 3.7. "Standard separation procedure".

3.1. Atmospheric dust on filters ; dry residue of atmospheric precipitations (fall-out)

Ashes + 90 mg Sr

| + HF

EVAPORATION

Residue SiO_2 volatilizes

+ NaOH

KOH

FUSION

+ HCl

DISSOLUTION

+ NH_4OH (pH 9.5)

CENTRIFUGATION

Residue   Solution

discard   + Na_2CO_3

(contains the Pu)

CENTRIFUGATION

Residue   Solution

See : "Standard   discard

separation procedure"   (contains the Cs)

(paragraph 3.7.)
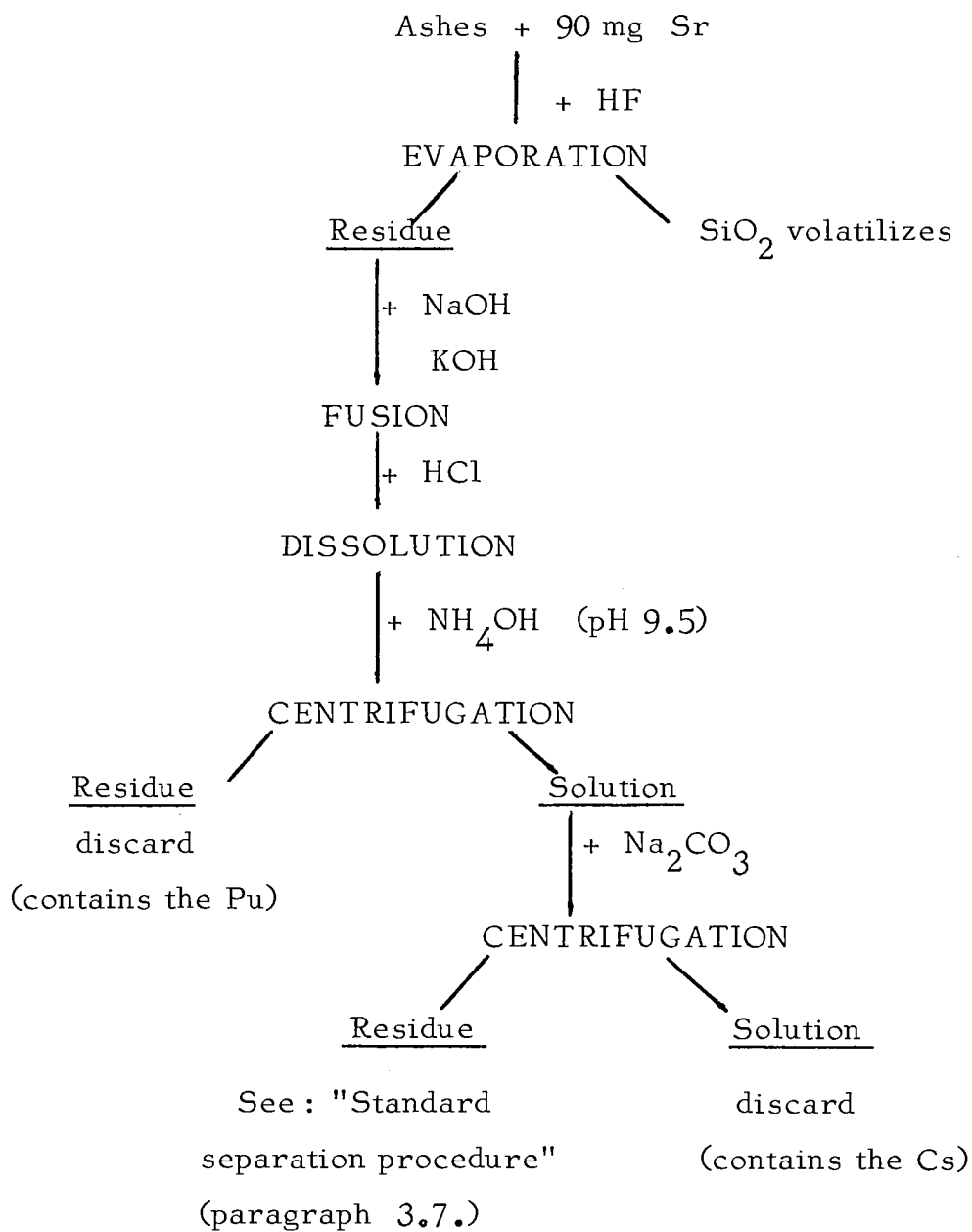
3.2. Fresh water (large volumes - ion-exchange resins method)

1. Place the water in a suitable vessel and add the strong cationic resin (Dowex 50-x 8, form H^+) in fairly small beads (200 - 400 mesh (1)) using about 1 - 3 g (wet resin) per litre of water (the amount of resin can be determined exactly if the cation concentration in the water is known).

2. Stir the water for 15 hours with an electromagnetic or rod stirrer. Let settle for one hour and siphon off the water.

3. Transfer the resin into a column of appropriate size and elute with about 500 ml of 3 N HCl per 100 g of resin.

4. Add 90 mg of strontium-carrier to the eluate and concentrate it to about 30 ml by evaporation on a sand bath.

5. Dilute to at least 500 ml, add 6 N NaOH until the phenolphthalein changes colour and then a saturated solution of Na_2CO_3 until precipitation is complete. Centrifuge and discard the solution.

6. See paragraph 3.7. "Standard separation procedure".

---

(1) Units of the Tyler Standard Screen Scale.

3.2. Fresh water (large volumes - ion-exchange resins method)

Water + Dowex 50-x8 resin

|

STIRRING

(15 hours)

|

SETTLING

Water — discard

Resin — transfer to column

+ HCl 3 N

ELUTION

Solution

Resin — recover

+ 90 mg Sr

+ NaOH 6 N

+ Na_2CO_3

CENTRIFUGATION

Residue

See : "Standard separation procedure" (paragraph 3.7.)

Solution

discard

(contains part of the Cs)
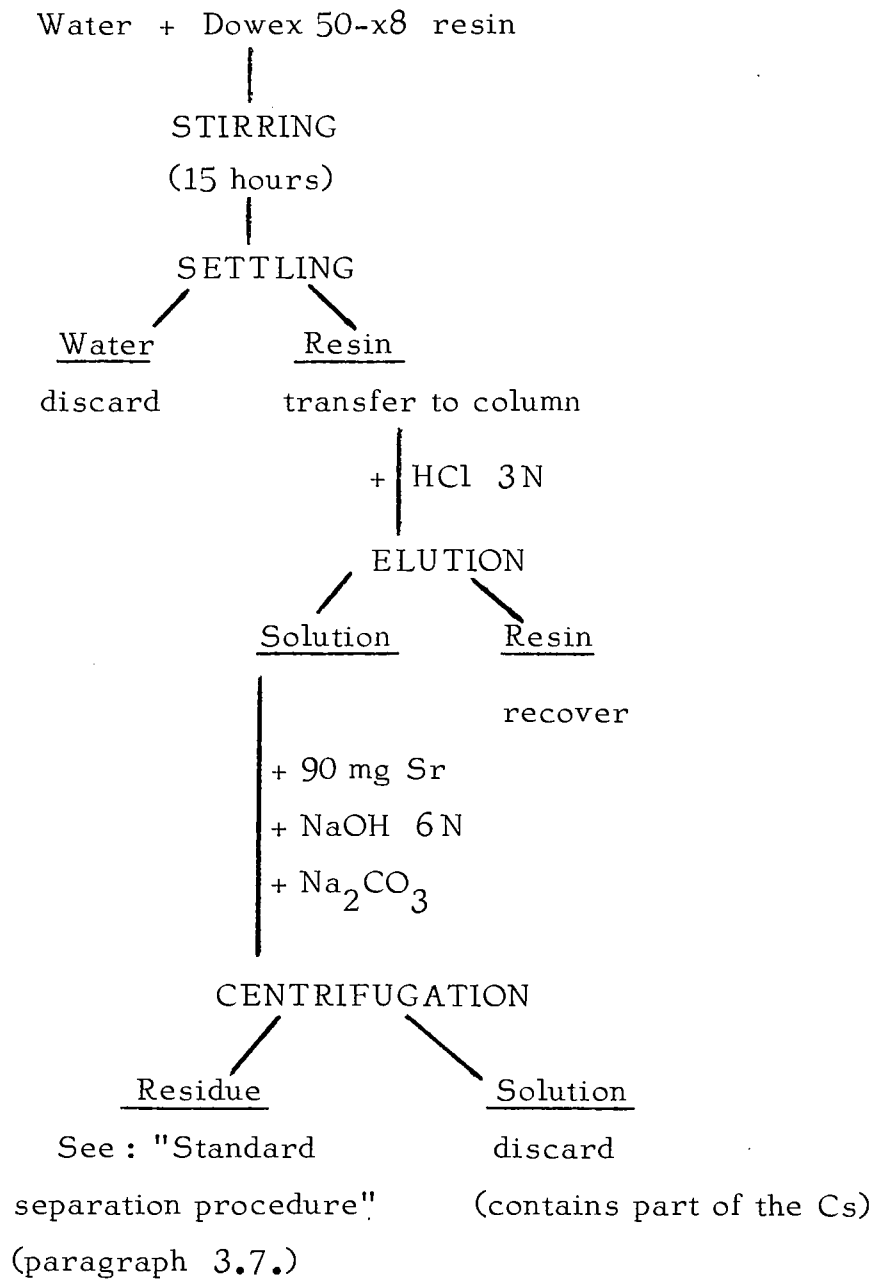
3.3. Milk, fish, whole diet

1. Add 90 mg strontium to the ashes and dissolve them with 65% HNO_3 and water (approx. 1:1).

2. Filter any carbonaceous and / or siliceous residue - which should in any case be very small - and discard it. Dilute the solution to about 500 ml.

3. Transfer to a 1000 ml centrifuge flask, add 2 ml of conc. H_3PO_4, then 6 N NaOH until the phenolphthalein changes colour, and centrifuge. Discard the solution, which can be used for the determination of cesium.

4. See paragraph 3.7. "Standard separation procedure".

3.4. Herbage, vegetables

1. Add 90 mg strontium to the ashes, moisten them with water and add about 30 ml of conc. HCl and the same amount of conc. HNO_3. Evaporate to dryness in porcelain or silica dish, by means of an infrared lamp or sand bath.

2. Remoisten the residue with 20 ml of conc. HCl and again evaporate to dryness, then continue heating for a few minutes.

3. Add a few drops of conc. HCl, just enough to moisten the residue, and allow to stand a few minutes, after covering the tray with a watch glass.

3.3. Milk, fish, whole diet

Ashes   +   90 mg Sr

|
| + HNO_3 1:1
|

DISSOLUTION

/   \

Solution   Residue

+ H_3PO_4 discard

+ NaOH

CENTRIFUGATION

/   \

Solution   Residue

discard   See : "Standard

(contains the Cs)   separation procedure"

                    (paragraph 3.7.)
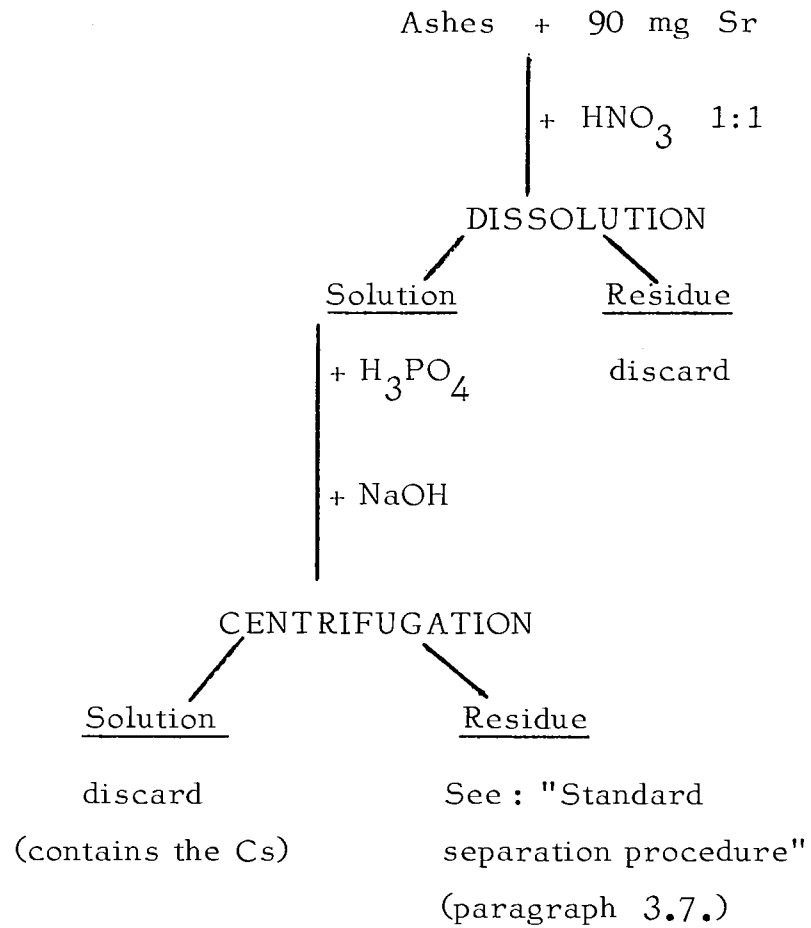
4.   Add about 50 ml of hot water and filter by suction through a low-porosity filter. Wash the residue with hot 5% HCl and discard it.

5.   Transfer the solution to a 1000 ml centrifuge flask, dilute to about 750 ml, add 2 ml conc. H_3PO_4 and 6 N NaOH until the phenolphthalein changes colour.

6.   Centrifuge and discard the solution, which can be used for the determination of cesium.

7.   See paragraph 3.7. "Standard separation procedure".

Note . The following is an alternative to steps 1 - 4 :

1.   Add 90 mg strontium-carrier to the ashes, then add 50 ml of conc. HF, 2 ml of conc. $HClO_4$ and evaporate to dryness, in a PTFE (polytetrafluorothylene) capsule on a sand bath.

2.   Add to the residue about 100 ml of approx. 30% HNO_3 and heat. Filter any residue by suction on a low-porosity filter. Repeat step 1. if the residue looks still abundant.

3.5. B o n e s   Bone ashes, after the addition of strontium-carrier (90 mg), can be treated straight away as described under "Standard separation procedure" (paragraph 3.7.).

3.4. Herbage, vegetables

Ashes + 90 mg Sr

$|$ + conc. $\begin{array}{l} HCl \\ HNO_3 \end{array}$

EVAPORATION

$|$ + conc. HCl

$|$ + hot H_2O

FILTRATION

Residue

silica : discard

Solution

$|$ + H_3PO_4

$|$ + NaOH

CENTRIFUGATION

Residue

See: "Standard
separation procedure"
(paragraph 3.7.)

Solution

discard
(contains the Cs)
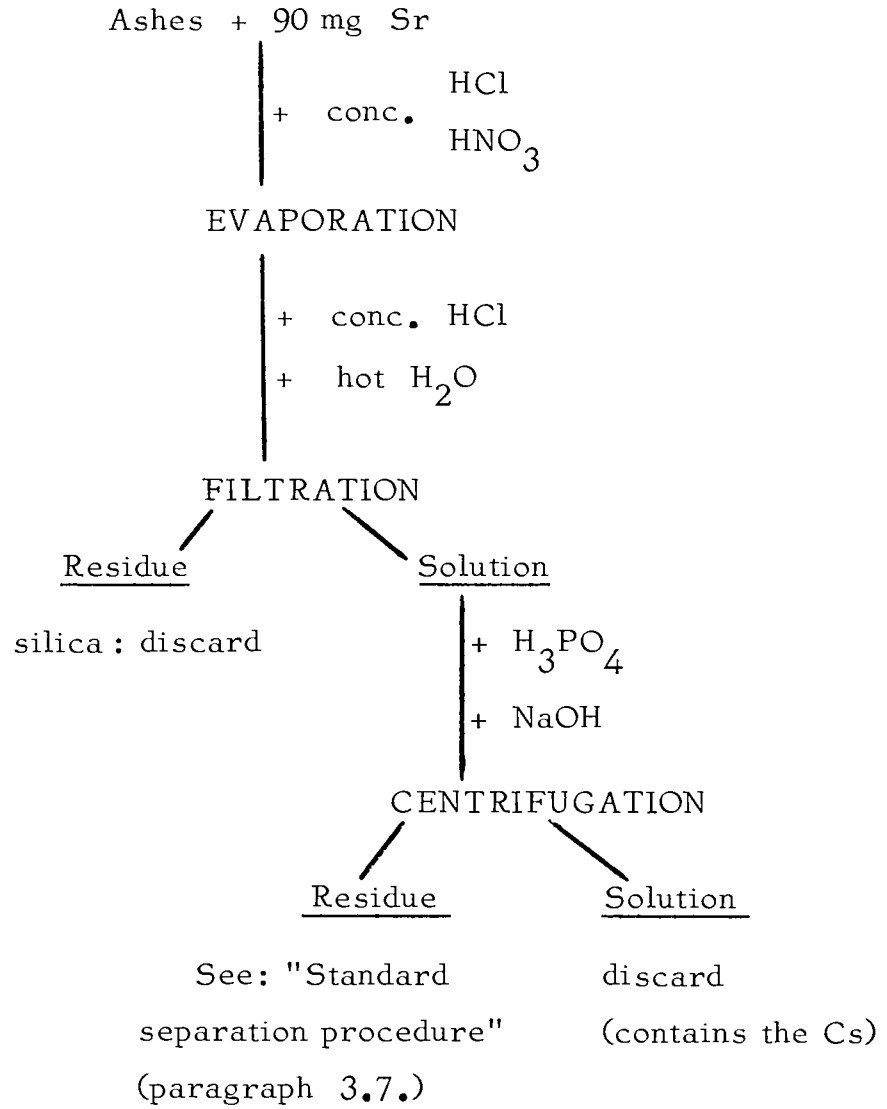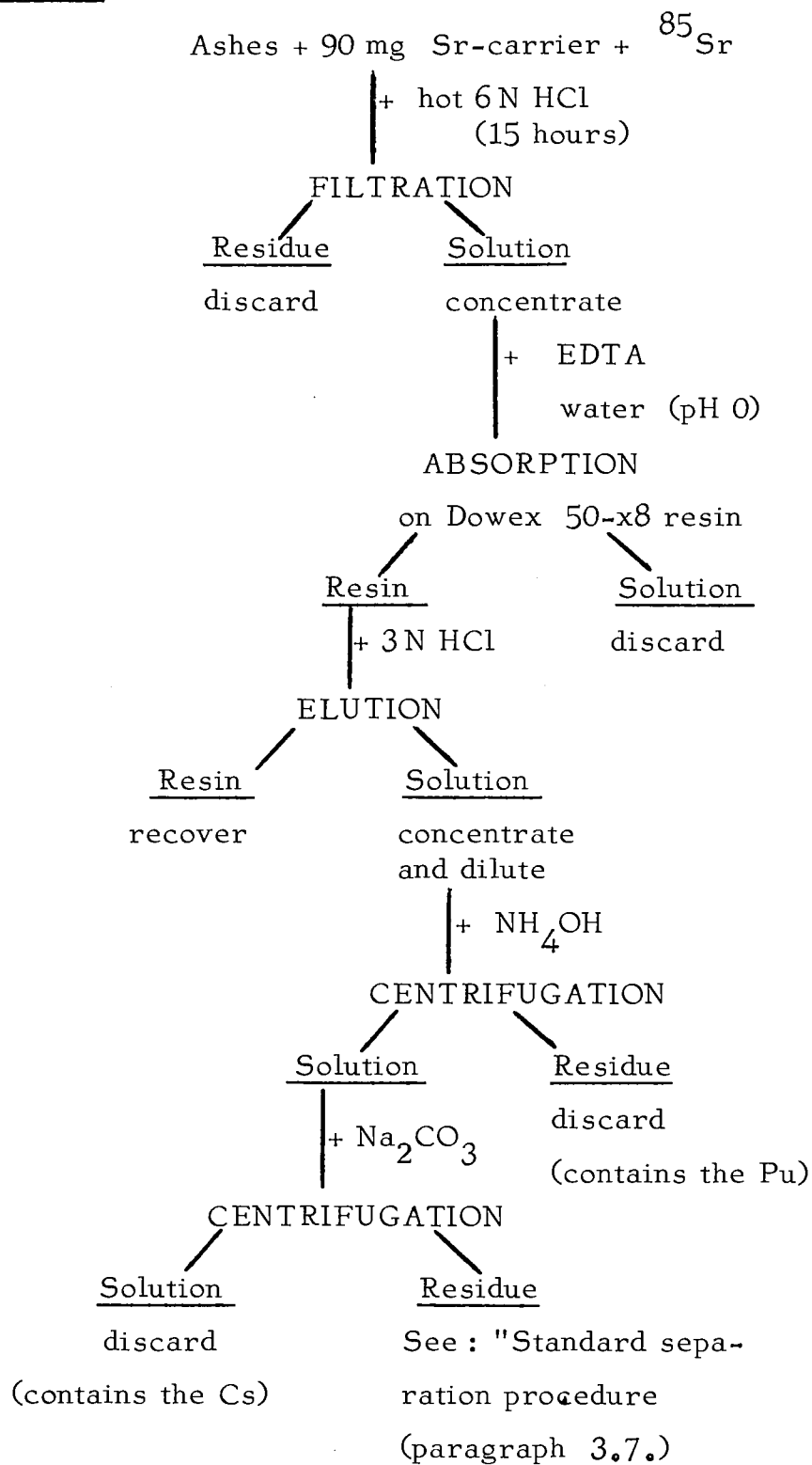
3.6. <u>S o i l</u> (1)

1. Only a few hours are required to ash soil samples, because of their low organic content. Transfer the ash into a 1 litre three-necked flask, equipped with a rod stirrer and reflux refrigerator (see Fig. 3).

2. Add 90 mg strontium-carrier, 5 to 10 thousand d/m (exactly-known) of Sr-85 tracer and 500 ml of 6 N HCl.

3. Heat overnight by means of a heating mantle, with the cooler and stirrer in operation.

4. Filter by suction on glass fibre filter and wash the residue, discontinuing suction and remixing, until a fine, white or grayish powder is obtained. Discard the residue, which consists mainly of SiO_2 crystals.

5. Evaporate the solution down to 100 - 150 ml, then dilute 1:6 with water, thus obtaining a solution of approximately N HCl because of the formation of the azeotrope. With the diluting water add an amount of EDTA (2) to have it 0.1 M in the final solution.

---

(1) For further details on soil analysis see the paper by M.C. de Bortoli : "Metodi di analisi della radioattività del suolo", to be presented at the XIV Annual Meeting of the AIFSPR, Formia 29 - 31 May 1968.

(2) The EDTA (ethylenediaminetetraacetic) acid) may be dissolved with ammonium hydroxide, thus obtaining a nearly neutral solution.

3.6. S o i l

Ashes + 90 mg Sr-carrier + ^{85}Sr

+ hot 6 N HCl
(15 hours)

FILTRATION

Residue   Solution

discard   concentrate

+ EDTA

water (pH 0)

ABSORPTION

on Dowex 50-x8 resin

Resin   Solution

+ 3 N HCl discard

ELUTION

Resin   Solution

recover   concentrate
and dilute

+ NH$_4$OH

CENTRIFUGATION

Solution   Residue

+ Na$_2$CO$_3$ discard

(contains the Pu)

CENTRIFUGATION

Solution   Residue

discard   See : "Standard sepa-

(contains the Cs) ration procedure

(paragraph 3.7.)

6. Check at the pH-meter that the pH of the solution is 0 ,
    then pour the latter through two colums in series (a-
    bout 20 x 200 mm) filled with strong cationic resin
    (Dowex 50-x8) in the Na^+ form. The resin is used
    50/50 in fine (150 - 250 mesh (1)) and coarse (20 -
    50 mesh) beads, to avoid excessive flow reduction
    by employing solely fine resin (2). Keep the flow-
    rate at 1 - 2 ml/min.

7. Wash the column with about 30 ml of 1 N HCl, then
    with 50 ml of water and successively elute them se-
    parately with about 500 ml of 3 N HCl.

8. Put the eluates together and evaporate the solution
    to about 50 ml, then dilute it and add NH_4OH until
    a pH of 9.5 has been reached.

9. Centrifuge and put the solution aside. Dissolve the
    residue with the minimum amount of conc. HCl, dilute
    and reprecipitate the hydroxides as in the preceding
    step.

10. Centrifuge and discard the residue, which can be used
    for the separation of plutonium. Put together the two
    solutions (this and that obtained in step 9), add 50 ml
    of a saturated solution of Na_2CO_3 and heat almost to
    boiling.

---

(1) Units of the Tyler Standard Screen Scale.

(2) The amount of resin used here is largely sufficient for the quan-
     tity of cations extracted from the soils processed (roughly 20 %
     by weight of total salts) ; it should be proportionately increased
     if the amount of cations extracted is consistently higher.

11.   Allow to cool, check that the precipitation is complete and centrifuge. Discard the solution, which may be used for the separation of cesium.

12.   See paragraph 3.7. "Standard separation procedure".

3.7. Standard separation procedure

1.   Dissolve the precipitate of carbonates or phosphates in the minimum quantity of 65% HNO_3. To the solution obtained add, slowly and cautiously, a double volume of 99% HNO_3.

2.   Leave to cool in waterbath for about 30 minutes, then centrifuge and discard the solution ; care must be taken to remove as much of it as possible from the precipitate and from the test-tube.

3.   Redissolve the precipitate in 20 ml H_2O and add 45 ml of 99% HNO_3 as described above. Repeat step 2.

4.   Into the same centrifuge tube add 50 ml of 99.5% acetone and stir, mechanically for 15 minutes (1).

5.   Centrifuge for 15 minutes and discard the solution.

6.   Repeat steps 4. and 5. (2).

---

(1)   The strontium-calcium separation by means of acetone is based on the work by P.E. Williams and H.T.Briscoe, Chem. News, 145, 177 (1932) and by R.N. Shreve, C.H. Watkins and J.C. Browing, Ind. Eng. Chem. Anal. Ed., 11, 215 (1939).

(2)   This method yields a residue of $Sr(NO_3)_2$ with a mean Ca content of less than 15% by weight. This contamination will not interfere in the determination of strontium by flame spectrophotometry.
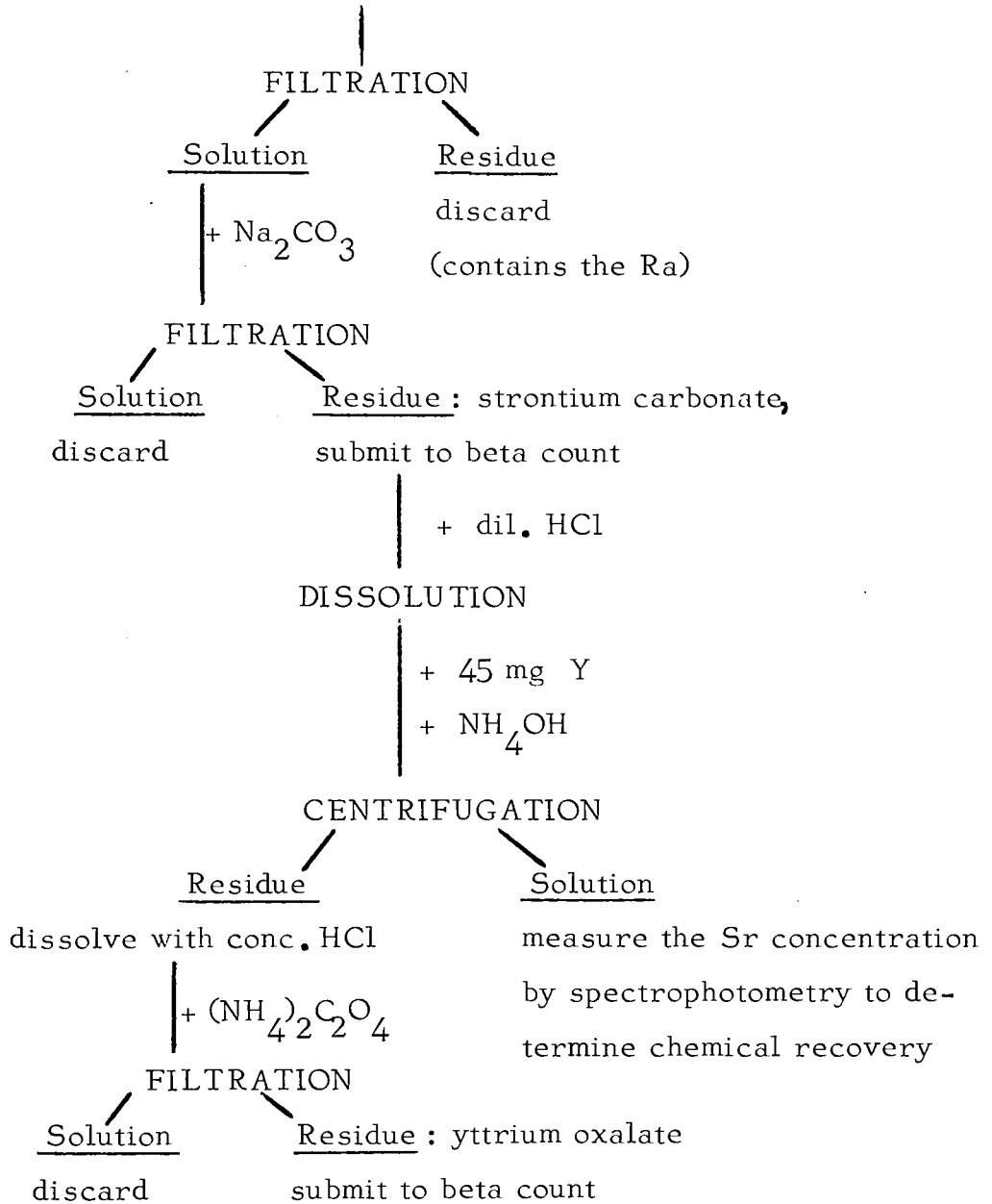
7. Redissolve the $Sr(NO_3)_2$ residue in about 40 ml H_2O, add 5 to 10 mg Y and NH_4OH until the phenolphthalein changes colour, keeping the solution in water bath.

8. Centrifuge and discard the precipitate. Add to the solution 2 ml of 6 M CH_3COONa and 6 M CH_3COOH until a reading of 5.5. is reached at the pH-meter (about 0.5 ml). Add 1 ml of 0.3 M Na_2CrO_4 and 10 mg of barium-carrier (1).

9. Filter on a medium porosity filter and discard the precipitate, which can be used to determine the Ra.

10. Add to the solution a further 10 mg barium-carrier and 0.5 ml 0.3 M Na_2CrO_4. Repeat step 9.

11. To the solution, which at this stage amounts to about 80 ml, add 10 ml of a saturated solution of Na_2CO_3 and 2 pellets of NaOH. Allow to digest in waterbath for at least 30 minutes.

12. Cool and filter by suction on a 3-piece Büchner funnel, using low-porosity paper. Wash with 95% ethyl alcohol.

13. (2) Dry the filter under an infrared lamp, mount it on a suitable planchet (see Fig. 4) , attaching it by means of a ring and covering it with a very thin layer (0.9 mg/cm^2) of mylar. Submit to beta counting.

---

(1) With some soil and water samples the precipitation can occur before any addition of barium, owing to the presence of barium in the sample. In that case there is no need to add the 10 mg of barium-carrier.

(2) With soil samples this step is replaced by the following : Place the filter into a suitable vessel (e.g. small plastic box) and submitt it to gamma spectrometry, to determine the chemical yield through the recovered fraction of ^{85}Sr.

3.7. Standard separation procedure

Precipitate of carbonates or phosphates

$\quad\quad\quad\quad$ + $\quad$ conc. HNO_3

DISSOLUTION

$\quad\quad\quad\quad$ + $\quad$ 99% HNO_3

CENTRIFUGATION

Residue $\quad\quad\quad\quad\quad$ Solution

dissolve in H_2O $\quad\quad\quad$ discard

$\quad\quad\quad\quad$ + $\quad$ 99% HNO_3

CENTRIFUGATION

Solution $\quad\quad\quad\quad\quad$ Residue

discard $\quad\quad\quad\quad\quad$ stir with acetone

CENTRIFUGATION

Residue $\quad\quad\quad\quad\quad$ Solution

dissolve in H_2O $\quad\quad\quad$ discard

$\quad\quad\quad\quad$ + $\quad$ 5 mg Y

$\quad\quad\quad\quad$ + $\quad$ NH_4OH

CENTRIFUGATION

Residue $\quad\quad\quad\quad\quad$ Solution

discard $\quad\quad\quad\quad\quad\quad$ + $\quad$ CH_3COONa

$\quad\quad\quad\quad\quad\quad\quad\quad\quad$ + $\quad$ CH_3COOH (pH $\approx$ 5.5)

$\quad\quad\quad\quad\quad\quad\quad\quad\quad$ + $\quad$ $Na_2Cr_2O_4$

$\quad\quad\quad\quad\quad\quad\quad\quad\quad$ + $\quad$ 10 mg Ba

3.7.   contd.

FILTRATION

Solution   Residue

+ Na_2CO_3 discard

(contains the Ra)

FILTRATION

Solution   Residue : strontium carbonate,

discard   submit to beta count

+ dil. HCl

DISSOLUTION

+ 45 mg Y

+ NH_4OH

CENTRIFUGATION

Residue   Solution

dissolve with conc. HCl   measure the Sr concentration

by spectrophotometry to de-

+ $(NH_4)_2C_2O_4$ termine chemical recovery

FILTRATION

Solution   Residue : yttrium oxalate

discard   submit to beta count

14. When the measurements are completed (normally after a fortnight), redissolve the precipitate in 5% HCl, washing the filter carefully (1).

15. Dilute to about 50 ml, add 45 mg of purified yttrium-carrier (2) and heat until all the CO_2 is removed. Transfer into a 100 ml centrifuge tube.

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(1) It is possible to check the radiochemical purity of yttrium and calculate the strontium-90 activity by a number of measurements performed on the $SrCO_3$ precipitate only (even in presence of strontium-89) (*) If it is desired to adopt this procedure, the following steps are to be omitted, with the exception of the determination of the chemical yield. This, of course, does not apply to soil samples where the strontium-85 tracer has been added.

(*) See: E. Van der Stricht, M. de Bortoli; P. Gaglione and A. Malvicini, Paper presented at the Conference on Low Level Radioactivity Measurements, London, 5 - 6 July, 1965.

(2) The natural radioactive contaminants can be separated as follows (Report NYO-4700 (Rev) : Manual of Standard Procedures, Health and Safety Lab., U.S.A.E.C. (1962))

Dissolve 16.85 g of $YCl_3.6H_2O$ in 60 ml of H_2O ; transfer into a 500 ml separatory funnel and add 60 ml of a saturated solution of NH_4NO_3 and 120 ml of tributyl phosphate (TBP). Shake for 5 minutes, allow the two phases to separate and collect the acqueous phase (the lower one) in a 500 ml separatory funnel. Extract this again with 80 ml TBP and put the two organic fractions together, discarding the aqueous fractions.
Back extract yttrium in 100 ml H_2O, agitating for one minute ; repeat this extraction with 70 ml H_2O, put the two aqueous phases together and strip with 25 ml CCl_4 to remove all the residual TBP. Standardize the yttrium solution by weighing the oxide (Y_2O_3).

16. Add concentrated NH_4OH until the phenolphthalein changes colour and centrifuge. Keep the solution.

17. Redissolve the precipitate with a few drops of conc. HCl, dilute to about 40 ml, and reprecipitate the yttrium hydroxide as in the previous step.

18. Centrifuge, and add the solution to that obtained in step 16. Acidify with conc. HCl and dilute to 100 ml in a volumetric flask. Take an aliquot of 1 ml, dilute to 100 ml and measure the strontium concentration by flame spectrophotometry, to determine the chemical recovery (1), as described under paragraph 6.3.

19. Redissolve the precipitate from step 18. with a few drops of conc. HCl, dilute to about 70 ml, add 8 ml of a saturated solution of $(NH_4)_2 C_2O_4$ and NH_4OH (diluted 1:1) until the methyl red changes colour.

20. Digest in water bath for 30 minutes, then cool and filter by suction on a 3-piece Büchner funnel, using low-porosity paper. Wash with 95% ethyl alcohol.

21. Submit the precipitate to the procedure described under step 13.

---

(1) For soil samples the chemical yield determined at step 13. (see foot-note) must be considered. The value obtained from the spectrophotometric measurement can be used to find the concentration of stable strontium in the soil (see paragraph 5.4. under "Determination of stable strontium").

4 - SEPARATION OF CESIUM [1]

4.1. Introduction   The introductory remark of section 3, concerning the size of the sample, holds also for the separation of cesium.

The concentration of cesium-137 in the samples can be determined by direct gamma spectrometry, provided that there are no interferences due to other radionuclides with gamma rays of energy close to that of cesium-137 (0.66 MeV).

When such radionuclides are present the cesium-137 determination can still be effected with reasonable accuracy by the spectrum-stripping technique provided activities of the interfering nuclides are not too high compared to that of cesium-137.

Otherwise, and where the specific activity of cesium-137 is too low, as in many samples, the separation procedure described below may be used to gain sensitivity. In fact, not only is the final precipitate radiochemically pure,but, in addition, its size being much smaller than that of the original sample the efficiency is nearly doubled.

4.2. Preparation of the samples   The solution containing the sample, set aside during the separation of strontium, is ready for the cesium separation except that it must be diluted and the pH checked and, if necessary, adjusted ; the pH value should be between 1 and 2 for HNO_3. The dilution required is of no set value, depending on the salt content of the sample (see below). As an order of magnitude a volume of two litres may be assumed, which may be considerably greater, however, for soil samples. Consequently, it is advisable, during the development

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[1]   For further details on this subject see the paper by E. Van der Stricht :"Détermination rapide du cesium-137 des retombées radioactives au moyen de phosphomolybdate d'ammonium", Radiochim. Acta, 3, 193 (1964), from which most of the material reported here has been taken.

of the procedure to determine the dilution necessary for each matrix.

This can be done by determining the separation yield for a certain volume of solution and then diluting until a quantitative yield is found. The yield can in turn be determined either by adding as a tracer an.other cesium isotope to the solution or by filtering twice the solution on AMP without varying its volume.
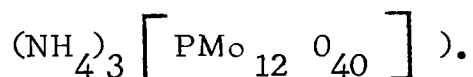
In the latter case, if X is taken to be the cesium content in the sample and R the separation yield, we have for the two runs

$$X = R A \qquad \text{and} \qquad X - A = R B$$

where A and B are the quantities of cesium separated in the two successive filtrations. From the two equations above we obtain

$$X = A^2 / A - B$$

4.3. Preparation of the AMP layer (ammonium phosphomolybdate $(NH_4)_3 \left[PMo_{12} O_{40} \right]$).

This operation requires particular care because an incorrectly prepared layer may cause losses of cesium.

1. Prepare a three-piece Büchner funnel with a low-porosity filter-paper, inserting a thin (2 - 3 mm) disc of synthetic sponge between the bored disc of the funnel and the filter, so as to ensure uniform filtration over the whole filter area.

2. Weigh a quantity of AMP corresponding to about 30 mg/cm^2 of filter area (e.g. for a filter of diameter 40 mm

about 400 mg AMP should be weighed out).

3. Suspend the AMP in 0.01 N HNO_3 and pour the suspension into the funnel.

4. Filter slowly by suction and, without letting the filtering dry, add 0.01 N HNO_3 with a wash-bottle until there is a column a few cm high of perfectly transparent liquid above the layer of AMP. At this point, if desired, the suction may be stopped.

5. Any AMP remaining afloat owing to surface tension is removed by dipping a piece of filter paper.

4.4. Filtration of the samples   Filter by suction the solution referred to under 4.2. through the AMP layer, taking care not to disturb it, e.g. by the turbulence caused by pouring the liquid into the funnel. Dismantle the funnel and collect from the lower inner rim of the top section of the funnel any traces of AMP, by means of a small piece of filter paper, which is then laid on the AMP layer.

Under the conditions described and with the samples cited here, the cesium separation by the AMP layer is quantitative, so that there is no need for a yield measurement on each sample (see 4.2.). A point that should be noted, however, is that the cesium separation yield will be lower if ammonium ions are present in the solution, as these compete with the cesium ions for capture by the AMP. It is therefore advisable to keep strictly to the suggested working conditions, including those for preparation of the solution (see section 3, strontium separation).

The filter with the AMP layer can be submitted to gamma spectrometry or to beta counting. In the latter case allowance must be made for the possible presence of potassium-40 and rubidium-87, naturally radioactive nuclides, and also of fission products. It is there-

fore necessary, in such cases, to accertain the radiochemical purity of the sample obtained. It should further be noted that the fission products (mainly ^{95}Zr and ^{95}Nb) are in colloidal form, so that pre-filtration on a low-porosity filter usually suffices to remove them.

Since the 0.66 MeV gamma rays are emitted by the metastable barium-137 into which cesium-137 decays, it is necessary to wait some 30 minutes for equilibrium to be established before effecting the gamma measurements.

4.5. <u>Fresh water</u> With this material the cesium separation can be effected directly on the water (provided, of course, the pH is adjusted to the recommended value) and the problem here is that of filtering large volumes (50 - 100 litres). To prevent clogging, the water should be prefiltered before passing on to the AMP layer. This can be done very conveniently by using a double Büchner funnel (see Fig. 5), with the first stage of larger diameter thant the second one, which holds the AMP layer. The first stage can be fitted with a glass-fibre or membrane filter, which can be replaced when the water flow-rate becomes excessively low.

With certain types of water, unusually rich in organic substances and/or biological organisms, even the process described above may prove ineffective and produce incomplete separation yields. The following process can be adopted in such cases :

1. After acidifying the water to pH 1 with HNO_3, stir and filter it, using a large-area (several hundred cm^2) glass-fibre filter.

2. Prepare an AMP layer of about 100 cm^2 (about 3-3.5 g)

and pass the prefiltered water through this (1).

3.　　After filtering, transfer the AMP to a beaker, using a wash bottle containing dilute NaOH ; continue adding the latter until dissolution is complete and the pH about 10.

4.　　Heat and add 5 - 6 g of $Ca(NO_3)_2 \cdot 4H_2O$, dissolved in about 100 ml H_2O. Heat to boiling and wash the $CaMoO_4$ precipitate with 100 ml of 0.001 N NaOH. Discard the precipitate.

5.　　Acidify the solution to pH 1 with HNO_3 and pass it on to a standard AMP layer.

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(1)　Certain waters tend to reduce the AMP, which then changes its colour from yellow to green. To deal with such waters, add at step 1., besides HNO_3 , a 30% solution of H_2O_2 to the amount of approximately 1 ml per litre of water treated.

4.6. __S o i l__　Under certain conditions, cesium could be absorbed not quantitatively on the resin of paragraph 3.6., step 6., The following is an alternative procedure for the separation of cesium before the passage through the resin, which can be used also whenever the radioisotopes of this element are the only contaminants looked for in the soil.

1.　　Evaporate to dryness the solution of paragraph 3.6., step 4. and redissolve with 15 - 20 ml of conc. HNO_3 and hot water.

2.　　Filter and wash with hot diluted HNO_3. Discard the residue. Dilute to roughly 3 litres the solution, check the pH and pass through an AMP layer.

5 - SEPARATION OF PLUTONIUM (1)

The introductory remark of section 3, concerning the size of the sample holds also for the separation of plutonium.

5.1. Atmospheric dust on filters ; dry residue of atmospheric precipitation

1. Proceed as described in paragraph 3.1., steps 1. to 6., with the following changes :

   a) to determine the chemical recovery, add an activity of ^{236}Pu tracer roughly equivalent to that expected for plutonium in the sample ;

   b) perform the double hydroxide precipitation of steps 4. and 5. by addition of NaOH to pH 13, instead of NH_4OH to pH 9.5 . This is to avoid the precipitation of aluminium, keeping it soluble in the acid form (2).

2. Dry in the centrifuge tube the hydroxide precipitate and redissolve it in the minimum amount of conc. HCl. Add 10 - 15 ml of 6 N HCl and 0.5 ml of 0.5 N $NaNO_2$.

(1) For further details on this subject see the work by M.C. de Bortoli : "Radiochemical determination of plutonium in soil and other environmental samples", Anal. Chem. 39, 375 (1967).

(2) When the separation of both strontium and plutonium on the same sample is required, one may effect the double hydroxides precipitation with NH_4OH first and successively that with NaOH.

3. Make the solution 9 N in HCl by addition of a suitable vo-
lume of conc. HCl and pass it through a plexiglass column
(see Fig. 6) about 10 x 100 mm filled with Dowex 1-x8
anionic resin, 150 - 250 mesh (1), in the Cl⁻ form and
previously washed with 10 to 15 ml of 9 N HCl. To speed
up the passage of the solution through the column vacu-
um may be used. The flow-rate however should not
exceed 0.5 ml/min.

4. Wash the column with 20 - 25 ml of 9 N HCl and discard
the absorption and washing solutions. Elute plutonium
with about 50 ml of a 6 N HCl - 0.2 N HF solution, col-
lecting the eluate in a PTFE (polytetrafluoroethylene)
beaker.

5. Add a few mg of NaCl , to keep as low as possible losses
due to adsorption on the beaker's walls, and evaporate
to dryness on a sand bath. If the residue looks white and
of the size of the added salt, proceed straight away to the
electrodeposition. However, normally a second ion-ex-
change step is required to obtain a proper deposit. In this
case repeat steps 2. through 4.

6. Dissolve the dry residue with 1 ml of water and 2 drops
of 12 N HCl and transfer it to the electrodeposition cell (2).
Wash the beaker with 4 ml of 6 N NH_4Cl and pour them into
the cell.

(1) Units of the Standard Tyler Screen Scale.

(2) The cell (see Fig. 7) consists of a plexiglass cylinder, about 80
mm long and 20 mm i.d., secured at the bottom by a stainless steel
screw stopper. This holds in place a 0.2 mm thick tantalum disc,
acting as the cathode. A rubber gasket is inserted between the disc
and the cell base. The electrodeposition apparatus consists of a
variable d.c. supply and of a motor (60 rpm), which drives the a-
node, a 2 mm diameter platinum rod spiral shaped at the lower end.
The electric connection at the cathode is provided by a metal plate
on which the cell is placed.

7.   (1) Place the anode end at 2 - 4 mm from the cathode and switch on the current keeping it approximately constant by means of the control knob at 2.5 - 3 A during 20 min. During this time the stirring motor must be operating.

8.   Add to the cell 1 ml of conc. NH_4OH, switch off the current and discard the solution. Wash gently, but thoroughly the cathode, then take it out of the cell, dry and submit to the alpha measurement.

Remark :   The procedure described yields, also from soils, essentially weightless plutonium sources, hence suitable for alpha spectrometry measurements.

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(1)   The electrodeposition conditions adopted here are described in the paper by R.F. Mitchell, Anal. Chem. 32, 326 (1960)

5.2. S o i l

1.   Proceed as described in paragraph 3.6., steps 1. through 10., with the changes mentioned in paragraph 5.1., step 1.

2.   Follow the procedure in paragraph 5.1. from step 2. forth.

6 - DETERMINATION OF STABLE STRONTIUM

6.1. Introduction With the exception, perhaps, of atmospheric dust and precipitation samples all the materials analysed for environmental monitoring purposes contain appreciable concentrations of strontium. This fact may cause substantial errors in the evaluation of the chemical yield, performed by means of carrier determination, if too little strontium was added to the sample. On the basis of the known values of stable strontium concentrations in the different materials, if 90 mg of strontium are added the error on the chemical yield should not exceed 5%, except in the case of large volumes of surface water and of soil samples where the error may be larger. Another method for the determination of the chemical yield is that based on the addition of a tracer, generally ^{85}Sr, as described in this work in connection with soil samples.

In view, however, of the growing interest for the stable strontium determination, we give here a brief description of the procedure by which it can be carried out.

The amount of sample to be processed will be known, for the different matrixes, after a short experience. The quantity of strontium involved should be not less than one tenth of a milligram.

In water samples, that have been dried or concentrated (by evaporation or via ion exchange resins), the measurements can almost always be effected directly on the sample in solution as described further on, whereas other samples require at least partial separation of strontium. The alkaline, alkaline-earth and certain other elements present in the samples raise the background emission so far as to dwarf the actual strontium emission. Thus, if no strontium enrichment is performed, one has to determine a small quantity by subtraction from a considerably larger one, which obviously gives wider scope to error.

6.2. Separation procedure

1. With sample of milk, fish, total diet, grass, vegetables
   and bones the appropriate strontium separation procedu-
   res are applied as far as the "Standard separation pro-
   cedure", paragraph 3.7. (1). With water samples,
   as already stated, direct measurements can be effected.

2. Carry out steps 1., 2. and 3. of the "Standard separa-
   tion procedure", paragraph 3.7.

3. Dissolve the residue of strontium and calcium nitrates
   in about 100 ml of water, heat in water bath, add about
   10 ml of saturated solution of Na_2CO_3 and leave to
   stand over heat for about 30 minutes.

4. Filter by suction on a 3-piece Büchner funnel, remove
   the filter and place it in a suitable vessel (e.g. plastic
   box) and submit it to ^{85}Sr gamma measurement.

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(1) Strontium-carrier is, of course, not added ; instead, add an
exactly known quantity of 5 to 10 thousand dis/min of stron-
tium-85 tracer.

6.3. Measurement by flame spectrophotometry

1. Redissolve the final carbonate precipitate with hot 5%
   HCl, washing the filter carefully to effect quantitative
   recovery.

2. Dilute the solution so as to have roughly 3 to 6 ppm of
   strontium and measure at the wavelengths of 460.7,

455 and 467 mμ , with a slit width of 0.05 mm, using reference solutions of 3.0 , 5.0 , 8.0 and 10.0 ppm of strontium.

3. To an aliquot of the solution add exactly 3 ppm of standard strontium (e.g. to 50 ml add 100 μl of a solution containing 1500 ppm strontium) and measure the solution thus obtained at 460.7 mμ as described at step 2.

4. Calculate the strontium concentration in the solution with the following equation

$$C \text{ (mg/l)} = \frac{(D_1 - D_f) \cdot D_{sa}}{D_2 - D_1}$$

where D_1 represents the instrument-reading at 460.7 mμ for the solution of step 2. ;

D_f represents the mean of the instrument readings at 455 and 467 mμ for the solution of step 2. ;

D_2 represents the instrument-reading, for the solution of step 3. ;

D_{sa} represents the instrument-reading obtained with a 3 ppm standard strontium solution.

The concentration thus obtained is to be referred to the original concentration in the sample, after correction for the chemical recovery, determined in paragraph 6.2., step 4.

The procedure described, omitting the standard addition

and the background measurement and hence with a single measurement at 460.7 m μ, is used to determine the chemical recovery under paragraph 3.7., step 18.

6.4. <u>Strontium in soil</u>   The concentration of stable strontium in soil samples can be determined from the difference between the value of the chemical yield obtained by the carrier method and the value obtained by the tracer method. Specifically, if 100 g of soil are being processed, the strontium concentration is expressed by the following equation:

$$ C \text{ (mg/Kg)} = (\frac{Q}{R} - 90) \text{ x } 10 $$

where   Q   is the quantity of strontium (in mg) found by spectrophotometry

and   R   is the chemical recovery determined by the tracer method.

As against its convenience, the accuracy of this method is somewhat limited ; this is proved by the fact that at times slightly negative values are obtained for C. This is due mainly to two factors ;
1) the final value depends on two measurements (of the stable strontium and of the ^{85}Sr), each with its own error, and 2) the final values is obtained as the difference between two quantities which are normally considerably larger. It must also be clearly understood that only a part of the strontium is determined by this method, i.e. the part put into solution by the extraction with 6 N HCl (see the paper cited in note (1) under paragraph 3.6.).

The "total" concentration of strontium in soil can be de-

termined by direct spectrophotometry measurement of the solution obtained by decomposing 1 - 2 g of soil with conc. HF. The decomposition is performed evaporating the acid in a PTFE (polytetrafluorethylene) capsule in presence of a few ml of $HClO_4$. The experience gained with the sandy soils of the Ispra area has shown that, after a double evaporation to dryness with 20 - 30 ml of HF, practically complete dissolution is obtained by remoistening with HCl of medium concentration. The solution obtained in this way can also be used to determine the calcium and potassium concentrations.

7 - DETERMINATION OF CALCIUM

7.1. <u>Introduction</u>   The calcium concentration in the various materials can be measured directly on the ash solution. For this purpose it is only necessary to bring the solution used for the strontium separation to the right volume in a volumetric flask and take an exact aliquot (a hundredth, five-hundredth or a thousandth according to the case). This aliquot, appropriately diluted, is then used for the determination of calcium by flame spectrophotometry. In the case of soil and hay samples only, it is advisable to process an aliquot of the sample separately (see paragraph 6.4.), because it has been found that after the extraction described some calcium, and even more potassium, remain in the residue of these materials.

7.2. <u>Spectrophotometric method</u> Dilute the sample aliquot, obtained as described above, so that the resultant solution has a calcium concentration of approximately 3 - 6 ppm (mg/l). Experience will soon indicate the right dilutions to apply to the different types of sample.

The measurement is performed directly on an aliquot of the solution ; 3 ppm of calcium are added to another aliquot before measurement. This can be done without appreciably varying the original concentration in the solution, e.g. by adding to 100 ml of the latter 0.1 ml measured by micropipette, of a 3000 ppm standard calcium solution.

The measurements are carried out at 422.7 mμ using standard solution of 5.0 and 10.0 ppm calcium for calibration. Next, a background measurement at 417 and 429 mμ is effected on the addition-free solution.

The calcium concentration in the solution is calculated through the following equation :

$$C \ (mg/l) \ = \ \frac{(\ D_1 \ - \ D_f) \cdot D_{sa}}{D_2 \ - \ D_1}$$

where D_1 is the instrument-reading, for the addition-free solution ;

D_2 is the instrument-reading, for the solution with standard-addition ;

D_f is the mean of the instrument-reading at 417 and 429 mμ for the first solution ;

D_{sa} is the instrument-reading for a 3 ppm standard calcium solution.

Experience will show the matrices for which background measurement is unnecessary. The authors have found that with the calcium concentrations suggested above, only soil samples need background measurement.

From the concentration value in the solution and from the dilution factors and the quantity of sample processed, the calcium concentration in the sample can be calculated.

7.3. Complexometric method   An useful alternative to the spectrophotometric method, which entails the use of a relatively expensive instrument, is the complexometric method which can also work, in certain cases, as a check for the spectrophotometric measurements.

The sample is prepared as described under paragraph 7.1., except that, as this method is less sensitive, a larger aliquot is required. As the total quantity rather than the concentration of calcium is determined by this method, roughly 1 mg of calcium is needed, if the titration is effected with a microburette and a titrating solution of EDTA (ethylene diaminetetraacetic acid) - disodium salt - 0.01 M. In fact, since 1 ml of titrating solution corresponds to about 0.4 mg calcium, it is clear that about 2 ml, and therefore 1 mg calcium, will be needed to obtain sufficient precision in the titration.

The solution to be titrated must be at pH 10 - 11. The indicator used is murexide, 0.5% in KCl, which changes from wine-red to a deep blue.

In the matrices considered here there is a considerable amount of phosphorus as phosphate, so that if the sample solution is alkalized without due precaution, calcium phosphate would precipitate

in many samples. The solution to be titrated must, therefore, be properly diluted.

Furthermore, with samples where precipitation still occurs, even after dilution, an excess of EDTA - disodium salt must be added to the solution and, after raising the pH to 10 - 11, the excess must be titrated with a standard calcium solution. In this reverse titration the colour change is from deep blue to wine-red and is less sharp than in the opposite direction.

Another disadvantage of the complexometric method is that the strontium naturally present in the sample is titrated together with calcium ; however, it only represents a small fraction of calcium.

8 - DETERMINATION OF POTASSIUM

8.1. Spectrophotometric method   Potassium can be determined directly on the sample solution. For soil and herbage samples see the procedure described for strontium (paragraph 6.4.). It is worth adding, however, that in the case of potassium the completeness of the extraction, after decomposition with HF, has been checked experimentally by comparing the element concentrations determined by spectrophotometry with those determined by gamma spectrometry (see next paragraph). The potassium extraction being complete, it is reasonable to assume that calcium and strontium are extracted totally also.

The spectrophotometric determination of potassium in environmental samples which contain other elements with low

ionizing potential, call for very careful preparation so as to reduce the systematic errors deriving from the different emission intensity of potassium in the samples and in the reference solutions. Details on this topic will be found elsewhere (1). We need only recall here the practical findings of that work, which are the potassium concentration ranges involving the lowest systematic error. These concentrations are 2 - 10 ppm for milk samples, 6 - 8 ppm for grass and soil samples, and 8 - 12 ppm for fish samples. In the case of fish the measurement can also be performed in the range 1 - 2 ppm, provided that 80 ppm sodium are previously added to the sample solution and to the reference solution.

The calibration curve is established by measuring standard potassium solutions of 1.0, 3.0, 5.0, 7.0 and 10.0 ppm. The measurements are carried out at the wavelength of 767 mμ.

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(1)   See the paper : M. de Bortoli and P. Gaglione "Comparison of flame photometry and gamma spectrometry for the determination of potassium in environmental samples", Giornale di Fisica Sanitaria e Protezione contro le Radiazioni, 10, N° 2 (1966).

8.2. Radiometric method   Natural potassium contains a small percentage of the isotope ^{40}K, which is radioactive and emits beta particles and gamma rays. If the specific activity and quantity of the sample are sufficient, it is therefore possible to determine the potassium concentration by measuring the gamma rays (energy 1.46 MeV) emitted by it. This measurement can be effected on the dried or ashed substance by means of a scintillation spectrometer consi-

sting of a thallium-activated sodium iodide detector, connected to a
multichannel analyzer, which counts, over a given time the number of
pulses corresponding to the photoelectric peak at 1.46 MeV.

The disadvantage of this method is in its poor sensi-
tivity, so that roughly 2 g of potassium are needed to double the
spectrometer background ; but it has the great advantage of being
practically bias-free provided the photoelectric efficiency of the
spectrometer has been determined for each matrix. This can be
done by adding a known quantity of a pure potassium salt to the
samples and measuring the increase of activity registered at
1.46 MeV.

The gamma spectrometry method, which has the fur-
ther advantage of not destroying the sample, can be usefully em-
ployed as a check during the development of the spectrophotome-
tric method, as was done in the above mentioned work.

9 - DETERMINATION OF URANIUM

9.1. Introduction   The method reported here is the fluorimetric
one, which on account of the low specific activity of uranium, is
more sensitive than the method based on the alpha radiation mea-
surement.

Generally speaking, the fluorimetric technique, just
because of its high sensitivity, requires extreme cleanness and ac-
curacy in handling and preparing samples and this point can hardly
be over-emphasized, even if people not familiar with the technique

will judge it excessive.

The instrument used in our laboratory is of the transmission type and can accept either liquid or solid samples.

Our present experience concerns mainly the determination of uranium in liquid wastes, performed not directly on the liquid, but on pellets obtained melting an appropriate flux with its dry residue.

9.2. Preparation of the pellets   The pellets are obtained melting the flux into small platinum dishes of convenient shape and size to match with the instrument holder. We use dishes 15 mm in diameter and 3 mm in depth.(see Fig. 8).

Evaporate an adequate aliquot of the solution to be measured into the dish (dilutions may be pre-arranged so that the volume of the aliquot range between 0.05 and 0.2 ml) and to the dry residue add one dose (400 mg) of the flux. This can conveniently be made through a compression-sampler, consisting of a small tube, close at one end, into which the powder is compressed manually. The pellet is then pushed out by a small piston. The rest position of the piston, and hence the weight of the pellet can be varied continuously(see Fig.8).

With some experience on this device, one can dose the flux within a few milligrams of the selected weight.

The flux consists of 45% each of sodium and potassium carbonate and 10% sodium fluoride and melts at roughly 600°C. In order to keep low the variations of the blank, it is advisable that the flux be prepared in a relatively large amount (say 100 g).

The pellets prepared with this flux, will come cleanly out of the platinum dishes, which is an important requirement for a

transmission instrument.

The dishes with the residues to be measured and the flux are put into a furnace set at 600°C. After 5 minutes at the desired temperature, the dishes are with drawn and introduced into a dessicator to cool (half an hour). These times and temperature are not extremely important so far as they are the same for the unknown samples, the standards and the blanks.

9.3. <u>Measurement of the fluorescence</u>   With each sample series it is advisable to prepare in duplicate one blank and two standards of concentrations including those expected from the unknown samples. The best thing would be to have each sample, unknown,blank and standard, in triplicate for, frequently, it happens that out of three supposedly identical pellets two give rather close readings, whereas one presents a much larger deviation.

This procedure is recommended whenever a sufficiently large number of platinum dishes is available. The blank readings are taken first, then their fluorescence is zeroed by means of the blank control and the standards and the unknowns are measured.

The standard addition method, described for flame photometry, is used to correct for interferences. However, in order to keep the latter as low as possible, the lowest practicable range of concentration should be used (say, below 50 ng).

The lower limit found in our laboratory is represented mainly by the blank fluorescence, which corresponds approximately to 5 ± 1 ng of uranium.
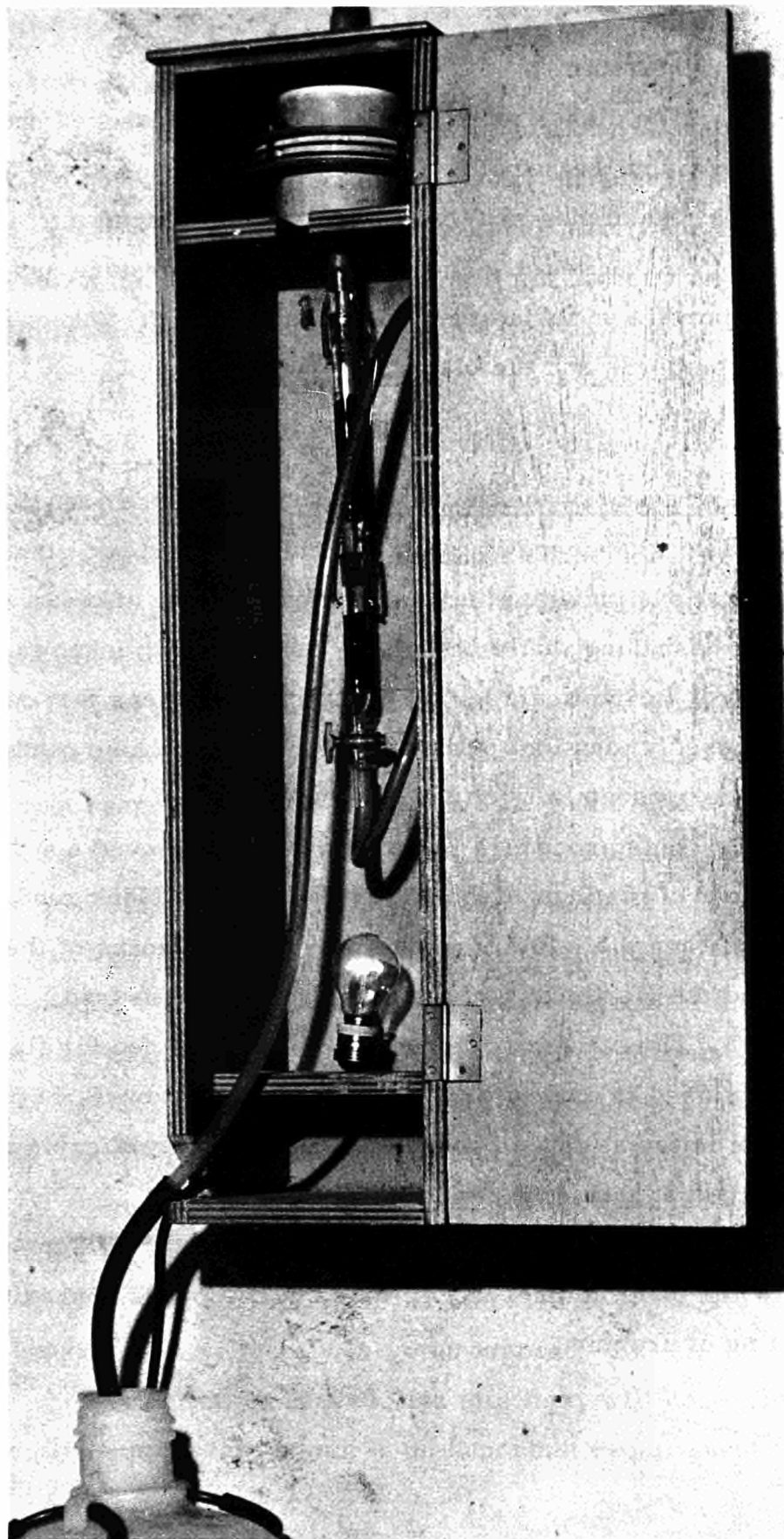
Figura   1   Raccoglitore di radioattività atmosferica : imbuto con filtro,
colonna di scambiatori di ioni e lampada di riscaldamento.

Figura 2   Utensili per il campionamento di suolo.
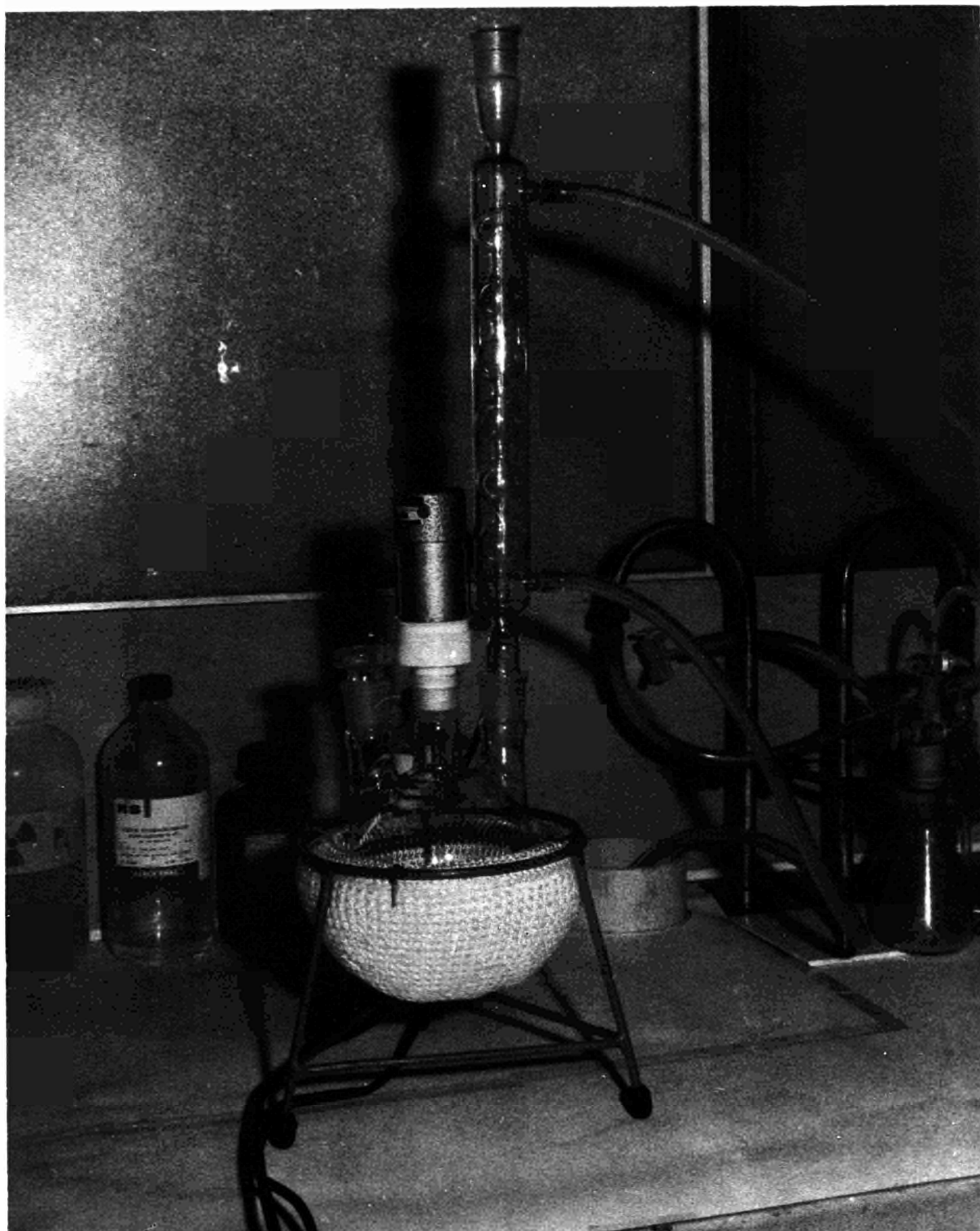
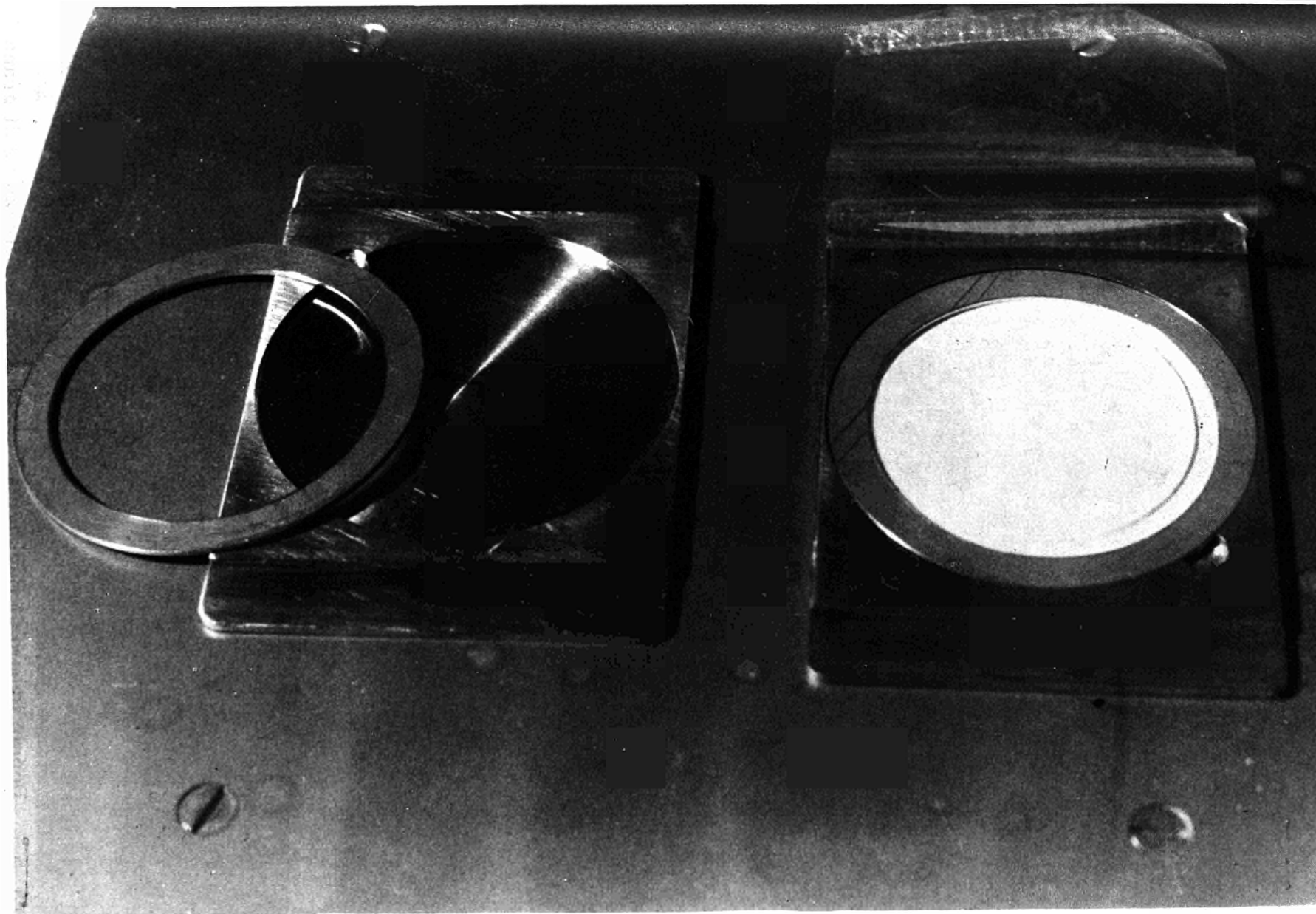Figura   3   Apparecchio per l'estrazione dei radionuclidi dal suolo.

Figura 4   Piastre di supporto e anello di copertura dei campioni di stronzio carbonato ed ittrio ossalato per il conteggio beta.

Figura 5   Doppio imbuto di Buckner smontabile per la filtrazione di grandi
volumi di acque su ammonio fosfomolibdato   (AMP).
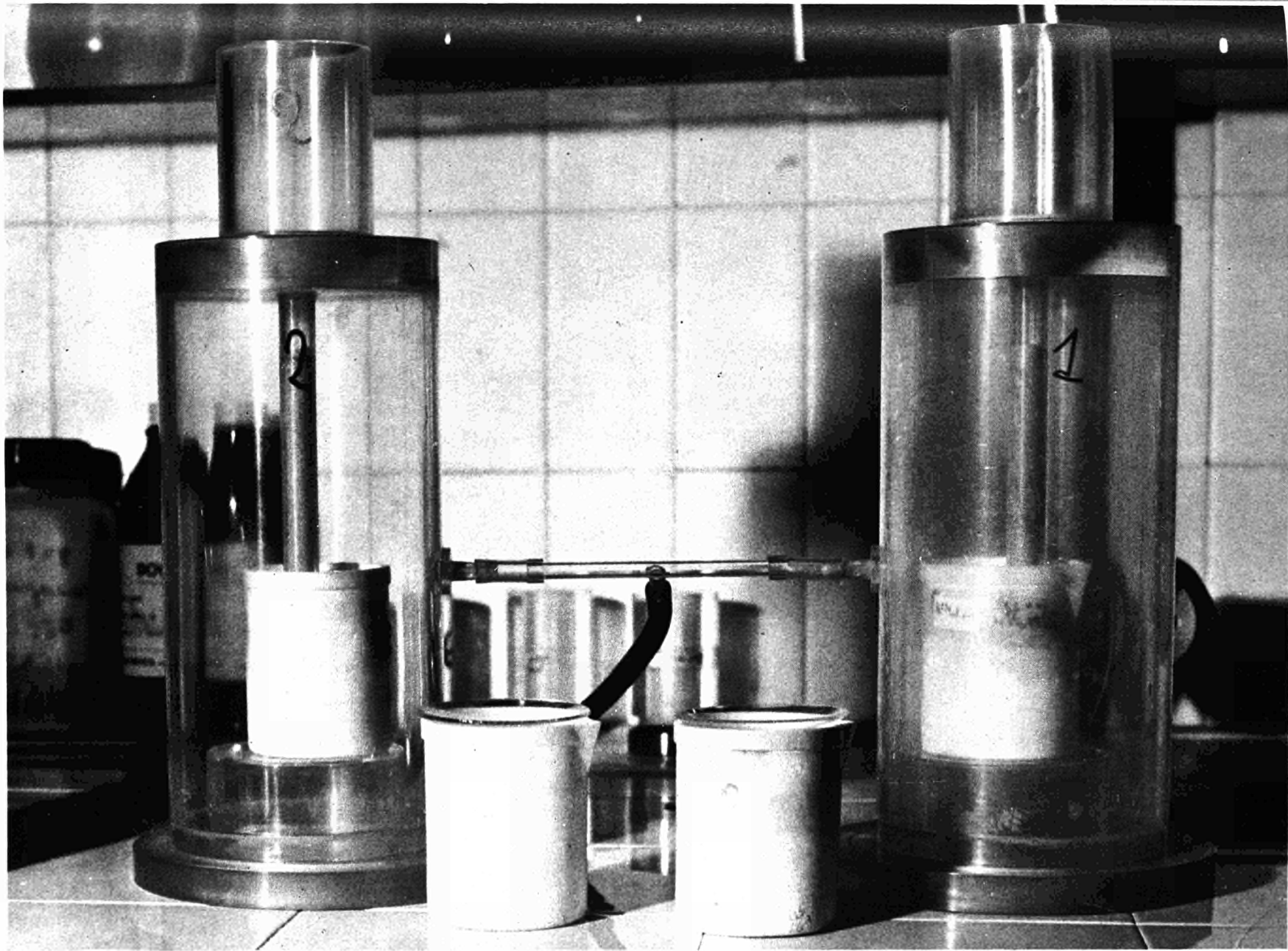
Figura 6   Separazione del plutonio : colonne con supporti per la filtrazione in depressione su resine a scambio ionico.
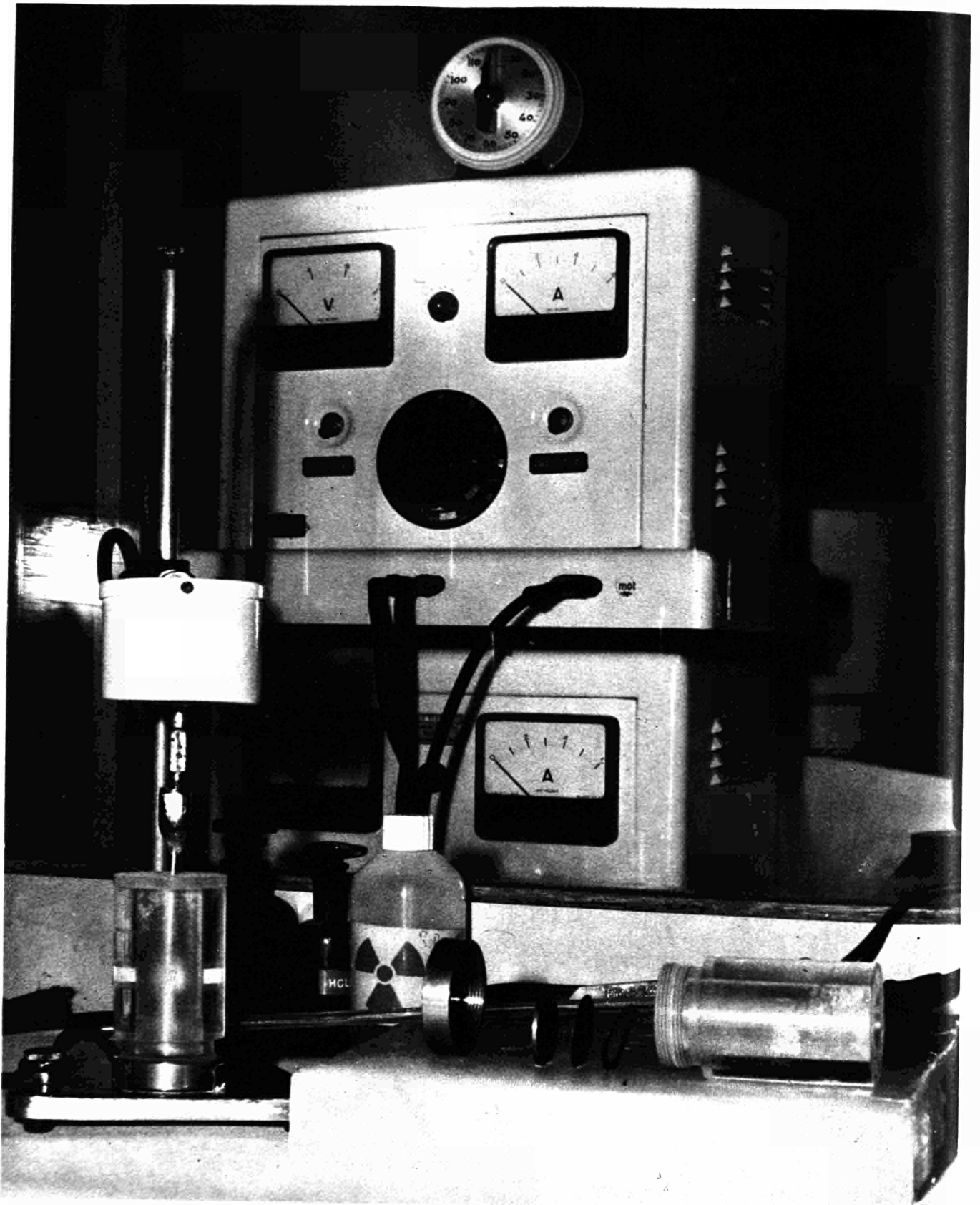
Figura 7 Separazione del plutonio : apparecchio di elettrodeposizione con dettagli della cella.
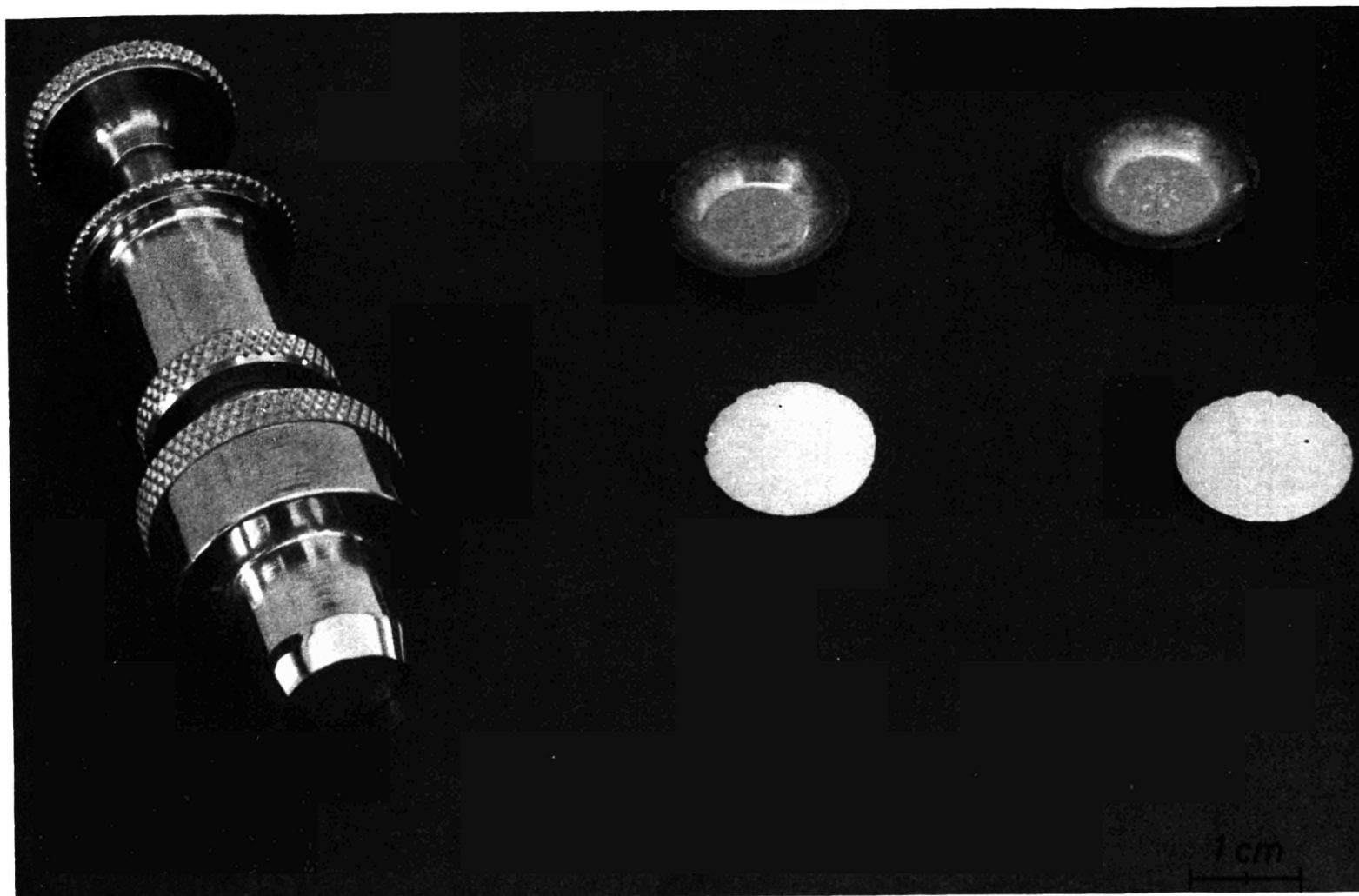
Figura 8   Determinazione dell'uranio : apparecchio di dosaggio a compressione, crogioli di platino e pastiglie pronte per la misura.
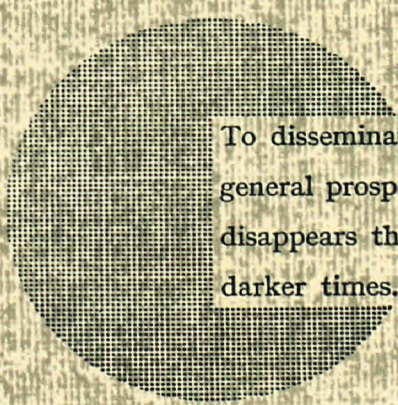
To disseminate knowledge is to disseminate prosperity — I mean general prosperity and not individual riches — and with prosperity disappears the greater part of the evil which is our heritage from darker times.

Alfred Nobel

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