

Chapter 14

Application of Cerenkov Technique to Continuous Measurement of Radioactive Isotopes Isolated by an Automatic Analytical Process

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INTRODUCTION

In an attempt to improve the radioisotope analyses made in our laboratory on the products of fission mixtures, we attempted the replacement of the classical radiochemical methods (separation, then measurement) by automatic methods in which a more sophisticated analytical process is followed by on-line measurement utilizing Cerenkov counting.

In the classical methods which are often manual, it is necessary to determine the chemical separation efficiency. This difficult determination is made by different techniques such as gravimetry, absorption spectrometry, etc. and when radiometric measurement is made (β or γ technique) the counting rate so obtained must be corrected and one is forced to consider factors such as detection efficiency, self-absorption and coefficient of geometry, decay scheme and radioactive equilibrium, quenching, etc.

In order to avoid these disadvantages we are conducting research, the object of which is the production of a liquid phase radioanalyser in modular form, allowing the continuous analysis of radioisotopes as they become isolated.

Figure 1 shows a block diagram of the radioanalyser. The separation unit at uniform concentration is designed around an analytical process, the object of which is to isolate one or more chemical elements. The detection unit which uses Cerenkov detection analyses on-line the corresponding radioisotope and the measurement is performed versus a standard of activity of the same radioelement, treated under identical experimental conditions.

After a short examination of the analytical methods used in the separation unit, we describe the technique employed in the detection unit and give some examples of its application.

THE ANALYTICAL PROCESS: SEPARATION UNIT

The process is based on the non-active isotope dilution method in conjunction with the substoichiometric separation principle, the theory of which was presented by Ruzicka.^{1,2}

The activity A of the radioelement to be measured can be determined from the separated activities (a) of the sample solution and (a_0) of a standard solution of the same

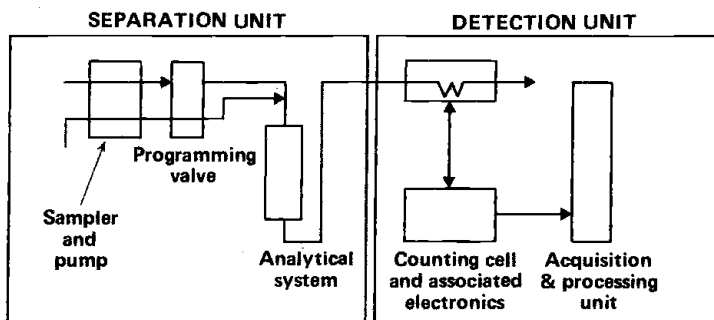


Fig. 1. Block diagram of the radioanalyser.

radioelement by the expression:

$$A = A_0 \frac{a}{a_0}$$

A_0 is the known initial activity of the standard solution.

This expression can be used and the analysis is then possible provided a number of conditions are satisfied:

1. The amount of carrier of the standard of activity must be minimal.
2. Exactly the same amount of isotopic carrier must be added to the two solutions.
3. A good isotopic exchange must be realized between the carrier and the corresponding radioelements.
4. For a correct evaluation of a and a_0 , an identical amount of the element in these two solutions must be isolated (the substoichiometric separation principle).

This method need not take account of the determination of chemical separation efficiency nor of the absolute determination of activity; it consists of a simple relative measurement. The separation processes used were:

- i) The substoichiometric separation with continuous solvent extraction.^{3,4}
- ii) The displacement at uniform concentration through cation exchange resins.^{5,6}

The dilution and substoichiometric separation are automatically made by the separation unit; it consists of a sampler, proportioning pump (Technicon), manifold, mixing coil, separation trap or ion exchange column.

RADIOMETRIC DETECTION: DETECTION UNIT

The problem, after continuous separation of the isotope to be measured at uniform concentration, was to perform an immediate radiometric measurement in order to profit from the presence of these isotopes without its parents and daughters; we did not need to take into account filiation and radioactive equilibrium. Therefore, we decided to adopt on-line measurement to avoid interference by decay products.

Choice of this method

The continuous measurement of β activity in fluid streams in chromatographic

effluents is a routine and useful technique in biological investigations;⁷⁻⁹ the principle and methods are applicable to any flowing stream such as that which comes out of the separation unit.

The various cells designed until now, belong to three groups:

Plastic scintillator cells. In this type of cell, the first to be described in the literature, the stream to be measured is circulated through a cell of plastic scintillator formed like a helix or a flat coil (SPF, NE 102 or NE 814).

Cells packed with suspended fluor particles. The most popular system is a cell filled with small anthracene crystals; the fluid flows in the spaces between the solid particles of fluor. Cells of this type are constructed of inert materials with low background and high light transmission.

Homogeneous counting systems. The fluid stream is continually mixed with a liquid scintillator before passing through the cell, made in low background material.

Note that the first and second types of cells cannot be used when the fluid stream is an organic solvent such as that used in continuous solvent extraction techniques. The third type of cell implies that the flowing solution be mixable with the scintillator; one is faced with exactly the same problems as in the discrete counting of aqueous samples by means of liquid scintillators, and chemical quenching is possible.

Since Belcher's first work,¹⁰ an important advance in methods of radioassaying solutions of β -emitting radionuclides has been achieved. This is also due to the development of liquid scintillation counting equipment, designed to detect very low intensity light pulses.¹¹⁻¹⁴

Among all the classic continuous counting processes, the use of the Cerenkov effect seemed to hold the most promise, so we decided to adopt this method, but if necessary we shall use γ detection or a homogeneous counting system.

The Cerenkov technique has been chosen for its simplicity, absence of chemical quenching, low background, relative selectivity as the result of energy threshold, and its possible application whatever the nature of the fluid stream and the possibility of reusing samples for subsequent investigations.

Detection unit

The β -counting equipment consists of a detection cell and an electronic unit with data acquisition accessories. Flow cells designed for the continuous counting of β -emitters should satisfy a series of conditions:

1. Their geometry must provide the highest possible collection of light by the photomultiplier.
2. The effective volume of the cell should be large enough for a good counting rate of the fluid stream, but to avoid loss of resolution this volume should remain compatible with the rate of change in radioactivity of the effluent stream.

A tubular cell of very low volume is used (500 μ l), formed like a W to obtain an instantaneous and correct evaluation of activity in the fluid stream at the output of the separation unit (Fig. 2). This cell may be constructed of glass or, more desirably, of quartz; the aqueous solution or the organic solvent which carries the radioelement is the radiative medium as much as are the walls of the cell.

The detection cell is placed in the median plane perpendicular to the axis of the two

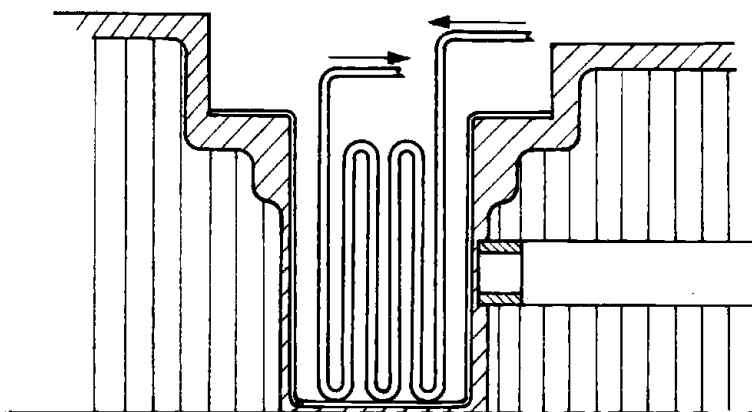


Fig. 2. Cerenkov detection: the continuous flow cell placed in the sample holder of Intertechnique SL 20.

photomultipliers of an Intertechnique liquid scintillation spectrometer model SL 20. This counting equipment is very simple to set up and to operate, and is economically priced, with good performance and reliability. The tubing used for inlets and outlets may easily act as a light pipe and so sufficiently long connecting lines made of opaque material such as black Teflon are used.

The highly directional nature of Cerenkov emission affects the light collection efficiency of a two photomultiplier system. It is useful to frost the walls of the cell to increase slightly the detection efficiency.

The relative selectivity of Cerenkov detection as the result of energy thresholds (~ 700 keV for water stream experimentally determined in our detection unit) recommended application of that technique for various complex counting problems; for instance, several radioisotopes corresponding to a radioelement obtained after chemical separation.

Weak β -emitters and α -particles are not counted. Counting efficiency need not be ascertained because the measurement is performed versus a standard of activity of the same radioelement, treated under the same experimental conditions.

One should also be aware of the fact that the efficiency of a flow cell is only a partial measure of its performance and that the sensitivity attained will depend on its volume and the flow rate of the liquid. Some detection efficiencies using standard solutions have been determined; the effective volume of the cell was determined by weighing and the efficiency was established by circulating a solution of known specific activity through the detector. The Cerenkov counting efficiencies for aqueous samples so determined are given in Table 1.

It should be noted here that for a fixed gain of the amplifier, the detection efficiency will greatly depend on a great number of parameters such as the form of the β spectrum of the nuclide, the geometric arrangement of the counting cell and the photomultipliers (light collection) refractive index of the cell and flow stream, optical properties of the solution (colour quenching), and the electronic setting of the sum and coincidence circuits.

We hope to increase the experimentally determined efficiency shown in Table 1 by changing the cell.

Table 1. Cerenkov counting efficiencies experimentally determined for some aqueous samples.

Nuclide	E_{max} (MeV)	Counting efficiency (% of disintegration)
Thallium-204	0.776 (98%)	2
Molybdenum-99	1.18 (83%)	7
	0.80 (3%)	
	0.41 (14%)	
Barium-140	1.02 (60%)	10
	0.48 (40%)	
Strontium-89	1.463	17
Praseodymium-144	2.996 (97.8%)	34
	2.30 (1.2%)	
	0.807 (1.0%)	

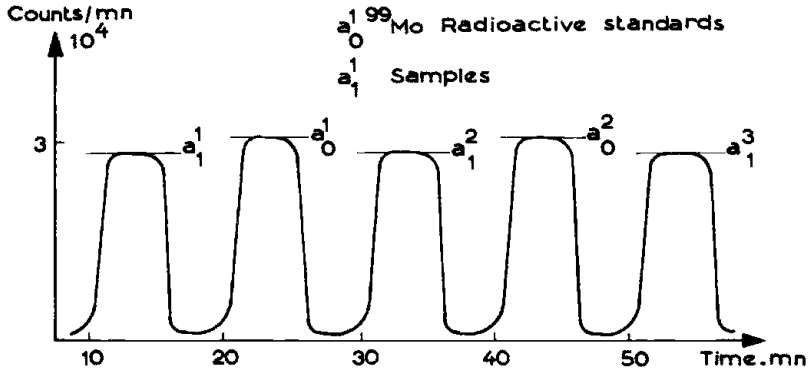


Fig. 3. Graphic recording of activity levels of analysis of molybdenum-99.

Data readout

The display of level of counting is performed on-line with a graphic recorder Servotrace Sefram, by means of a ratemeter Intertechnique model DA 101, so verification of performance is possible during the course of analysis. This graphic information is in the form of a series of activity levels corresponding to either sample or standard of activity (see Fig. 3). The liquid scintillation spectrometer model SL 20 is also specially equipped with a Teletype for data print out; the same information which is printed is also punched on tape. The punch tape output is an ideal interface for using the instrument with an off-line digital computer which makes a complete statistical treatment of the data.

The arithmetic means of several measurements (5 to 6 counting rates in general) determine the uniform level of activity corresponding to the sample or a standard isolated

Table 2. Sensitivity data.

Isotope separated from a mixture	Sensitivity ($\mu\text{Ci/ml}$)
Molybdenum-99	10^{-3}
Strontium-89	2.10^{-3}
Barium-140	10^{-2}
Yttrium-91	2.10^{-3}

at uniform concentration. The ratio of two successive levels (one for the sample, the other for the standard of activity) gives us the ratio $a:a_0$ of the general expression:

$$A = A_0 \frac{a}{a_0} \quad (\text{see p. 182})$$

It should be noted here that for such a comparative measurement done in a single detection cell, we need not take account of geometry, counting efficiency, branching decay or colour quenching; all these parameters are similar for sample and corresponding standard activities. Likewise, we are able to ignore on the one hand, radioactive decay, and on the other hand, radioanalyser drift, by making alternate measurements on sample and standard in short time intervals.

APPLICATIONS

Cerenkov counting was applied to automatic or semi-automatic analysis of molybdenum-99, strontium-89, barium-140 and yttrium-91. The analytical process of molybdenum-99 is based on continuous substoichiometric separation with solvent extraction and that of strontium-89, barium-140 and yttrium-91 is based on continuous displacement at uniform concentration through ion exchange resins.¹⁵

The reproducibility of the analysis is good; taking the example of molybdenum-99, we obtain after the complete analytical process a standard deviation of 0.3% at the level of 30000 c.p.m.; for strontium-89 and barium-140 we obtain 0.5% for the same counting rate. The maximum error on a ratio of activity is 1% at a confidence level of 95%. The total accuracy of the analysis depends overall on the standard of activity.

The sensitivity is now low: this is not on account of the Cerenkov counting efficiency but is due to the use of a flow cell of very low volume and the necessity for a great number of successive counting intervals in short periods of time to produce an instantaneous and correct evaluation of activity in the effluent stream. Some data of sensitivity are given in Table 2.

It should be noted here that these automatic analyses with on-line detection are more rapid (4 to 6 times) than the classic radiochemical method.

CONCLUSIONS

The on-line detection by Cerenkov counting of radioactive isotopes as they are isolated is a practicable and useful technique in our automatic analytical process based on the substoichiometric separation in conjunction with non-active isotope dilution.

In comparison with classic continuous measurements of activity in fluid streams by

scintillation methods, the Cerenkov counting provides a great number of advantages, i.e. simplicity, easy handling of samples, possibility of using organic solvents and reusing samples for subsequent investigations.

The measurement is performed versus a standard activity of the same radioelement treated under the same experimental conditions; it consists of a simple comparison between two count rates whose ratio is equal to the specific activity ratio of the two flowing streams which is in turn identical to the ratio of the initial activities. We need not take into account several factors which one is forced to consider when making absolute measurements or a measurement on a classically isolated sample.

The time of analysis of a sample has been decreased, the sensitivity of analysis is now low but repetitive performance is good.

This process of radiochemical analysis may be extended to the measurement of trace impurities using radioisotope dilution.

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REFERENCES

- 1 J. Ruzicka and J. Sary, in *Substoichiometry in Radiochemical Analysis* (Ed. M. Williams), Pergamon Press, Oxford, 1968.
- 2 J. Sary and J. Ruzicka, *Talanta* **18**, 1 (1971).
- 3 J. Ruzicka and M. Williams, *Talanta* **12**, 967 (1965).
- 4 J. Ruzicka and J. Sary, *Talanta* **8**, 228 (1961).
- 5 B. Tremillon, *Les Séparations par Résines Echangeuses d'Ions*, Gauthiers-Villars, Paris, 1965.
- 6 J. Colomer, M. Cousigne and G. Mezger, *Le Déplacement et ses Possibilités d'Application à l'Analyse de Radioélément par Dilution Isotopique*, Rapport CEA R 4100, 1971.
- 7 K. Piez, *Nuclear Chicago Tech. Bull.* **15** (March 1964).
- 8 E. Rapkin, *Bulletin Pickernuclear* **11**, 6L (May 1967).
- 9 E. Schram, in *The Current Status of Liquid Scintillation Counting* (Ed. E. D. Bransome), Grune and Stratton, New York, 1970.
- 10 E. M. Belcher, *Proc. Roy. Soc. (London)* **A216**, 90 (1953).
- 11 K. von Haberer, *Atomwirtschaft* **10**, 36 (1965).
- 12 M. M. Ross, *Anal. Chem.* **41**, 1260 (1969).
- 13 R. P. Parker, *Digitechniques Tech. Rev.*, Inter technique, Paris, 1969.
- 14 R. P. Parker and R. H. Elrick, in *The Current Status of Liquid Scintillation Counting* (Ed. E. D. Bransome), Grune and Stratton, New York, 1970, p. 110.
- 15 J. Colomer, M. Cousigne and G. Metzger, *International Symposium on Rapid Methods for Measurement of Radioactivity in the Environment*, Neuherberg, 1971, I.A.E.A., SM 148/10, Vienna.