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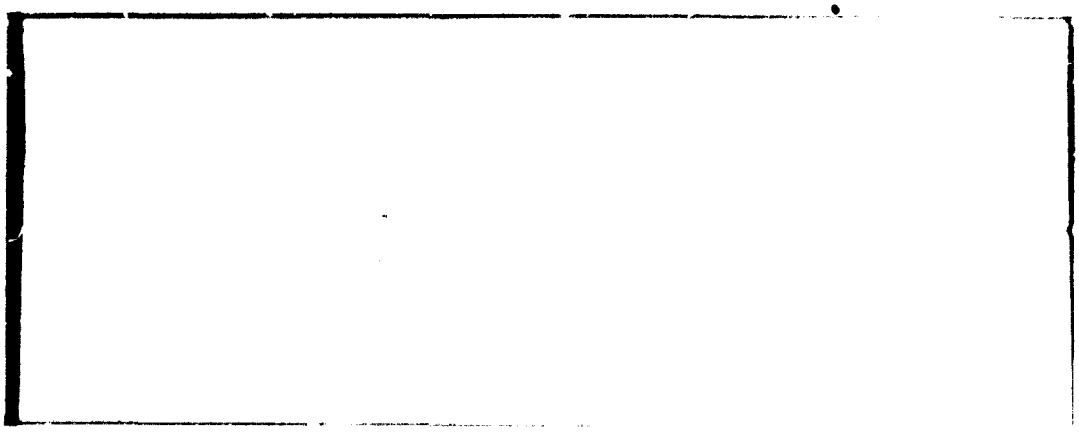

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ISOTOPIC ANALYSIS OF CARBON AND NITROGEN BY MEANS OF A 2 MV VAN DE GRAAFF (*)

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Summary

The possibilities offered by the nuclear reactions :

$^{12}C(p, \gamma)^{13}N$ $^{14}N(p, \gamma)^{15}O$
$^{13}C(p, \gamma)^{14}N$ $^{15}N(p,\alpha\gamma)^{12}C$

to estimate the isotopic concentration ratios $^{13}C/^{12}C$, $^{15}N/^{14}N$ or $^{15}N/^{12}C$ were studied experimentally.

Two kinds of gamma detector [Ge(Li) and NaI(Tl)] were used. It is evident that in view of its resolution the former is more discriminating (separation of neighbouring lines), but our results show that the use of a large NaI(Tl) detector is necessary when large batches of samples have to be examined quickly.

Introduction

Mass spectrometry is undoubtedly the most accurate method available for the isotopic analysis of carbon and nitrogen but in many cases, for example the examination of solid or liquid biological samples, a previous chemical treatment of the specimens is necessary. From this viewpoint nuclear methods offer a useful alternative because the samples here can generally be analysed immediately without any special preparation. It is true that where precision of the measurements is concerned these techniques cannot compete with mass spectrometry, but their ease of application is a great advantage in the fast handling of very large batches of samples from isotopic tracer experiments.

The idea of measuring the isotopic concentration ratios $^{13}C/^{12}C$ and $^{15}N/^{12}C$ in biological media by direct observation of proton-induced nuclear reactions was put forward in 1971 by RICCI[1,2]. About two years later CLOSE and al.[3,4] published the results of a thorough if not exhaustive study of the use of this technique to determine the relative isotopic contents of carbon ($^{13}C/^{12}C$) and nitrogen ($^{15}N/^{14}N$).

Principle of the method

Table I lists the nuclear reactions usable for the selective determination of carbon-12, carbon-13, nitrogen-14 or nitrogen-15, together with their main characteristics, i.e :

- energies at which suitable resonances are found and the half-widths of these resonances ;
- cross-sections at the excitation function maxima ;
- energies of the most prominant gamma transitions.

The excitation functions of these nuclides obviously contain many other resonances, especially at energies above 1.8 MeV, but from this value onwards more and more elements under proton bombardment emit prompt gamma photons and the risks of interference increase accordingly.

The principle of the method lies in the detection of prompt gammas produced by the nuclear reactions of table I during proton irradiation of the samples, the intensities of the lines characteristic of the above-mentioned elements being proportional to their concentrations in the bombarded material.

Isotopic analysis of carbon

The theoretical possibilities and practical limits of the nuclear reactions :

$^{12}C(p, \gamma)^{13}N$ and $^{13}C(p,\gamma)^{14}N$

have been discussed by CLOSE and al.[3].

Experience shows that the best results are obtained with 600 to 800 keV protons beyond which, especially from 897 keV upwards, the measurements can be perturbed by the gamma radiation characteristic of nitrogen-15, relatively intense in view of the cross-sections involved. Under these conditions carbon-13 is determined very simply and reliably using the 8.061 MeV gamma transition. Figure 1 gives calibration curves established first with a 100 cm^3 Ge(Li) detector and secondly with a 102 x 102 mm NaI (Tl) counter.

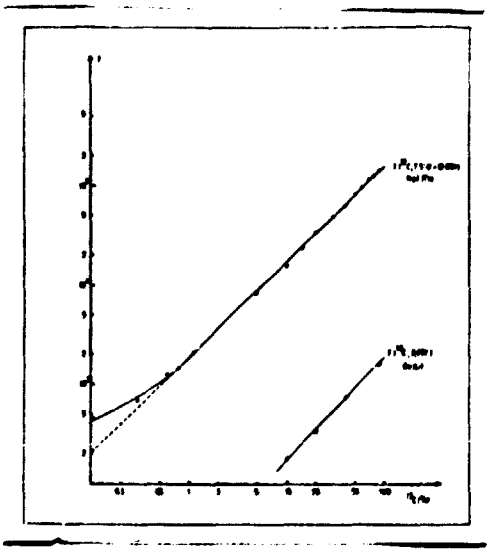

Fig. 1. Intensity of the characteristic carbon-13 line versus isotopic content of this element in barium carbonate.
Ep = 800 keV ; I = 0.05 µA ;
Q = 1000 µC
Detector-target distance about 25 mm.

Table I. Main characteristics of nuclear reactions suitable for the selective determination of carbon-12, carbon-13, nitrogen-14 and nitrogen-15.

Element considered	Nuclear reaction used	Resonance energies (keV)	Corresponding half-widths Γ (keV)	Maximum cross-section (mB)	Energy of most prominent gamma transitions (MeV)
Carbon-12	$^{12}C(p,\gamma)^{13}N$	456,8 ± 0,5	39,5 ± 1,0	0,127	2,366
		1698 ± 5	72 ± 9	0,035	3,509
Carbon-13	$^{13}C(p,\gamma)^{14}N$	551 ± 1	32,5 ± 1	1,44	8,061 ; 4,116 3,378 ; 2,370 2,313 ; 1,632
		1747,6 ± 0,9	0,075 ± 0,050	340	9,172 ; 7,028 6,444 ; 2,728 2,144
Nitrogen-14	$^{14}N(p,\gamma)^{15}O$	1061,6 ± 1,4	3,9 ± 0,7	-	8,283 ; 5,242 3,042
Nitrogen-15	$^{15}N(p,\alpha\gamma)^{12}C$	429 ± 1	0,9	200	4,439
		897,37 ± 0,29	2,0 ± 0,2	800	4,439
		1210 ± 3	22,5 ± 1	600	4,439
		1640 ± 3	68 ± 3	340	4,439

The determination of carbon-12 is less straight forward since the characteristic 2.366 MeV line is not isolated in the prompt gamma ray spectrum of a carbon target bombarded with such protons, certain carbon-13 lines being responsible for interferences. The first, at 2.370 MeV, is almost indistinguishible from the above owing to their natural widths. Secondly the 3.378 MeV transition, though relatively weak, gives rise to a satellite line at 2.356 MeV attributable to the double escape process (3.378-1.022) in the detector. Finally the 2.313 MeV line should not be neglected because its perturbing effect, especially when an NaI (Tl) detector is used, increases with the carbon-13 isotopic concentration.

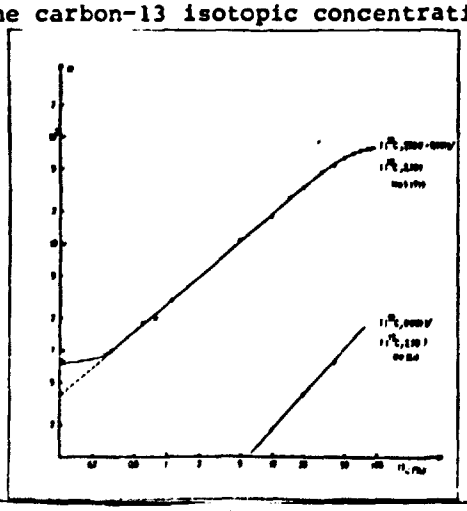

Fig. 2. Ratio of the characteristic carbon-12 and carbon-13 line intensities versus isotopic abundance of the latter. The experimental conditions are those of the previous figure.

Figure 2 shows examples of calibration curves concerning $^{13}C/^{12}C$ isotopic abundance measurements based on the estimation of the 8.061 and 2.36 MeV peak intensity ratio (the latter, as pointed out above, being in reality a complex mixture of several lines). These curves show clearly that although the Ge(Li) detector as expected, is apparently the more suitable for such analyses the NaI (Tl) counter can be useful for some isotopic measurements, especially at carbon-13 contents below 70 %. A point to emphasize in this respect is that while the former instrument is more selective because of its resolution, the latter, owing to its efficiency, reduces the measurement time by a factor 10 to 20. This is a serious advantage when large batches of samples must be examined quickly at costs competitive enough to warrant the use of these techniques in place of mass spectrometry.

Isotopic analysis of nitrogen

It is relatively easy to determine the nitrogen-15 content directly in a given substance by evaluating the intensity of the line at 4.439 MeV. This peak is so large that the analysis only takes 5 to 10 minutes, especially with an NaI (Tl) detector, as shown by the curves of Figure 3. The minimum concentrations measurable (1 to 10 $\mu g.g^{-1}$) become lower as the proton energy increases. The NaI(Tl) detector can also be used to estimate the isotopic concentration ratios $^{15}N/^{12}C$ as suggested by RICCI[1,2]. An example of a calibration curve is shown on Figure 4. However the background from the characteristic carbon-12 line (E_γ = 2.366 MeV), all the stronger as the nitrogen-15 content is high, limits the field of application of this technique to enrichments below 10 % ; moreover for the same reasons it is preferable to use an irradiation energy of 800 keV unless the nitrogen-15 concentrations are very low, when more energetic protons are called for. The Ge(Li) detector is obviously more accurate in view of its finer resolution but the analysis time is prolonged accordingly.

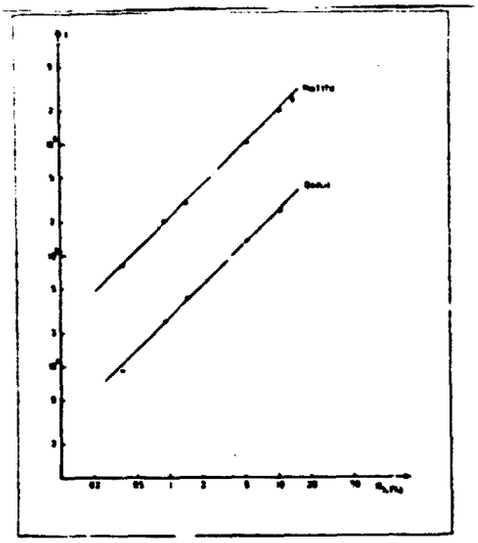

Fig. 3. Intensity of the characteristic nitrogen-15 line at 4.439 MeV versus isotopic content of this latter in urea.
Ep = 1100 keV ; I = 0.2 µA ;
Q = 1000 µC.
Detector-target distance about 25 mm.

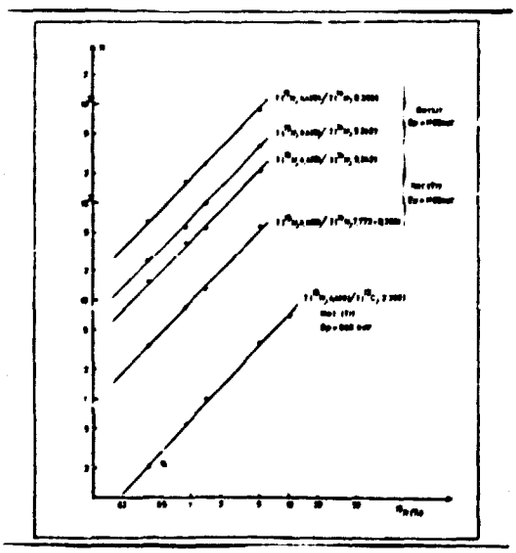

Fig. 4. Ratio of the characteristic line intensities for the two nitrogen isotopes (Ep = 1100 keV) on the one hand, carbon-12 and nitrogen-15 (Ep = 800 keV) on the other, versus isotopic concentration of the latter in urea. The other experimental conditions are those of the previous figure.

For the determination of the isotopic content ratio $^{15}N/^{14}N$ from the intensity of the corresponding characteristic lines (4.439 MeV for nitrogen-15 ; 5.242 and 8.283 MeV for nitrogen-14) these detectors are both suitable, as shown by the calibration curves of Figure 4. Since the yield of the nuclear reaction :

$$^{14}N(p, \gamma)^{15}O$$

is slight, it follows that the 5.242 and 8.283 MeV lines are weak compared with the very large peak at 4.439 MeV due to nitrogen-15. As a result, the optimum incident proton energy proves to be 1100 keV for the estimation of nitrogen-15 isotopic concentrations above the natural value, and 1250 to 1750 keV or higher still for levels much below 0.37 %. Once, the ^{15}N enrichment exceeds about 5 %, isotopic concentration ratios $^{15}N/^{14}N$ become very difficult or even impossible to measure. Concerning the analysis time, this ranges between a few minutes (5 to 10) with a large NaI(Tl) detector and some tens of minutes (50 to 100) with a Ge(Li) detector of reasonable volume.

Conclusion

Amongst the advantages of the above methods, the most important is clearly the fact that the products, whether solid or liquid, can be measured directly without previous chemical treatment.

The precisions obtainable lie in relative values between 5 and 10 % (2 to 5 % measuring carbon-13 or nitrogen-15 separately). This performance certainly cannot compare with that of mass spectrometry (10^{-3} to 10^{-2} %), but for isotopic tracer experiments requiring the analysis of very large batches of samples, these techniques offer valuable possibilities by virtue of their speed and simplicity.

The isotopic contents measurable range from :

- 0.1 to 90 % for carbon-13,
- 0.05 to 5 % for nitrogen-15.

Where quantities of matter are concerned, an analysis can be performed on a few 10^{-6} g, which means that these processes are especially useful for the examination of micro-samples such as biopsies for example.

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4. J.J. Malanify and D.A. Close, Nucl. Inst. Meth. 118, 293 (1974).