THE DETERMINATION OF CARBON, NITROGEN AND OXYGEN IN GASES BY NEUTRON TIME-OF-FLIGHT SPECTROMETRY

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Carbon, nitrogen and oxygen were determined in gases by time-of-flight spectrometry of prompt neutrons from the respective reactions $^{12}C(d, n)^{13}N$, $^{14}N(d, n)^{15}O$ and $^{16}O(d, n)^{17}F$, produced by a pulsed beam of deuterons of 2 MeV (for nitrogen) or 3 MeV. The analysis is non-destructive and requires about 15 min. per sample. The relative standard deviation for all three elements was about $\pm$ 3%. Detection limits, using a total irradiation current of 20 millicoulombs, for carbon, nitrogen and oxygen, respectively, were $6 \cdot 10^{-8}$ g, $2 \cdot 10^{-7}$ g and $1.7 \cdot 10^{-7}$ g per cm^2 cross-sectional area of irradiating beam.

Introduction

Among the more common elements for which neutron activation analyses are not sufficiently sensitive, are carbon, nitrogen and oxygen. These elements are so important that attempts to extend the advantages of nuclear methods of analysis to their determination are justified. One such attempt, in which the radioactive products of photoactivation with high energy gamma-rays was used to determine microgram quantities, has recently been reported[1]. In this work, another attempt is described, in which the prompt neutrons from (d, n) reactions are measured by neutron time-of-flight spectrometry.

When deuterons of energy, E_d, induce (d, n) reactions, the energy of the emitted neutron, E_n, is determined by the Q-value of the reaction and the angle Θ at which it is emitted. From the kinematics of a nuclear reaction, the neutron energy is given by

$$\sqrt{E_n} = v \pm \sqrt{v^2 + w} , \qquad (1)$$

where

$$v = \frac{\sqrt{m \, m_n \, E_d} \cos \Theta}{(m_n + M)} \qquad (2)$$

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and

$$w = \frac{MQ + E_d(M - m)}{(m_a + M)} \, . \tag{3}$$

m, m_n and M, respectively, refer to the mass of the deuteron, the neutron and the product nucleus.

The most accurate method available at present for neutron spectroscopy is the time-of-flight technique in which the time t (nanoseconds) taken by a neutron to cover a distance s (metres) is measured and related, non-relativistically, to the energy of the neutron, in MeV, by

$$t = \frac{72.3 \times s}{\sqrt{E_n}} \, , \tag{4}$$

where the constant includes the mass of the neutron and the relevant conversion constants. The energy resolution of a time-of-flight spectrometer, obtained from Equation 4, is given by

$$\frac{\Delta E_n'}{E_n} = \left[\left(\frac{\Delta t \sqrt{E_n}}{36.1 \times s} \right)^2 + \left(\frac{2\Delta s}{s} \right)^2 \right]^{1/2} \, , \tag{5}$$

where ΔE, Δt and Δs are the uncertainties in energy, time and distance, respectively. The uncertainty in a flight path of several metres is relatively small, so that the energy resolution of the system will depend largely on the precision in measuring the flight time, the time interval between two pulses, marking the start and end of the neutron flight.

When the irradiating deuteron beam consists of pulses of short duration, the arrival of a pulse at the target may mark the instant of neutron generation, and the arrival of the neutron at the detector may mark the end of the time-of-flight. Clearly, the duration of the irradiating pulse will introduce an uncertainty in the flight time, and constitutes a limitation of the method.

This technique[2] has already been applied to the determination of deuterium in gases[3] and to the isotopic analysis of calcium in thin deposits[4]. The determination of light elements in comparatively thick plates of metals has also been described using the same technique[5]. This paper describes the use of neutron time-of-flight spectrometry for the elemental determination of carbon, nitrogen and oxygen in gases.

The Q-values of (d, n_0) reactions on carbon-12, nitrogen-14 and oxygen-16 are given in Table 1, together with the calculated energies of neutrons emitted in the (d, n_i) reactions where the product nucleus is left in its i-th excited state. The detected neutrons will, however, be measured as a group with an energy spread about the calculated value, the extent of which is determined by the energy resolution of the spectrometer.

Table 1

Neutron energies from (d, n) reactions
$E_d = 3.0$ MeV $\Theta = 0°$

Target	Natural abundance, %	Q-value (d, n_0) MeV[6]	Neutron energy, MeV
^{12}C	98.89	− 0.281	2.582(n_0)
^{14}N	99.63	5.066	7.932(n_0)
			2.771(n_1)
			2.710(n_2)
			1.763(n_3)
			1.098(n_4)
			1.033(n_5)
			0.693(n_6)
			0.235(n_7)
^{16}O	99.759	− 1.627	1.223(n_0)
			0.685(n_1)

Experimental

The electronic equipment[7] was the same as used previously[3]. Because the neutron detector was sensitive to gamma-rays as well as to neutrons, signals caused by gamma-rays were rejected by pulse shape discrimination[8] and low level electronic noise by the energy discriminator. The efficiency of the neutron detector fell rapidly for neutrons below 1 MeV, while the detection threshold for neutrons was somewhat below 700 KeV.

The gas handling apparatus and the irradiation cell have been described[3]. Irradiations were carried out with the 5.5 MV Van de Graaff accelerator at the Southern Universities Nuclear Institute. Deuteron pulses lasted for 5 nsec. and were 400 nsec. apart. Low average beam currents, ranging between 0.7 and 1.2 μA, were used to prevent damage to the nickel window of the gas cell, which could not be cooled. For improved resolution, larger flight paths are necessary (see Equation 5), but as the count rate decreases with s^2, a compromise between resolution and the duration of the analysis has to be struck. At about 3 metres resolution was adequate, and the count rate sufficiently high to complete an analysis within 15 minutes.

Neutron spectra

Typical neutron time-of-flight spectra, obtained from methane, oxygen and nitrogen with 3.5 MeV deuterons, are given in Fig. 1. The energy scale is not linear, because the spectra are based on time measurements with channel number

proportional to the neutron flight time. For this reason, the peaks are spread over more channels towards the low energy ends of the spectra.

The peaks in the spectra correspond to the energies listed in Table 1, provided correction is made for the difference in deuteron energy and for the 160 KeV energy lost by the deuteron beam in the nickel window. Neutrons with energies
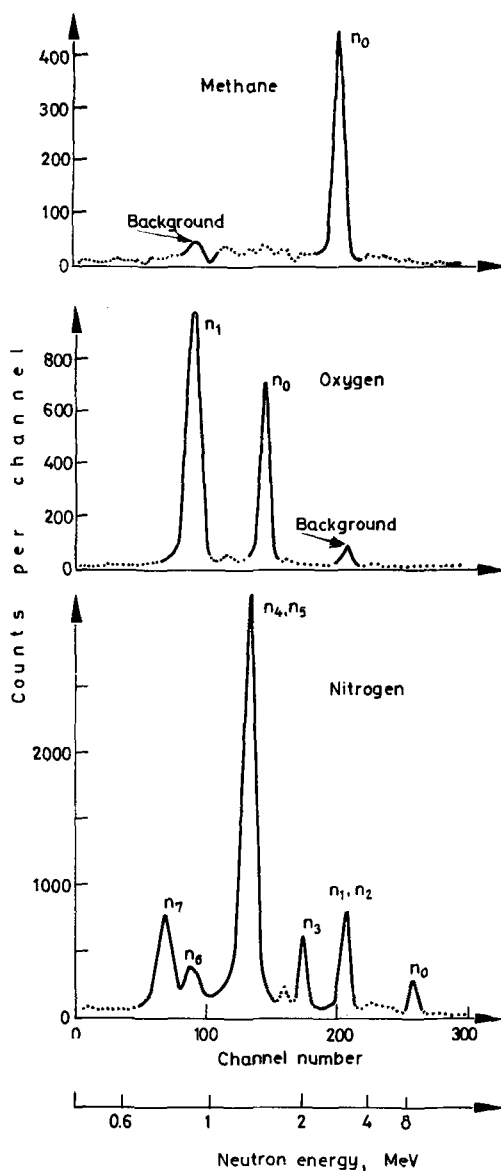

Fig. 1. Typical neutron time-of-flight spectra. $E_d = 3.5$ MeV, $\Theta = 30°$, $s = 2.99$ m

below 700 KeV could not be distinguished from gamma-rays by pulse shape discrimination. Accordingly, at lower deuteron energies, neutron groups which may have been expected from Table 1, with energies below this value, were not observed.

Carbon-12 produced only one characteristic neutron group which was used to provide a measure of the carbon content of the sample. By contrast, oxygen-16 gave rise to two neutron groups of which the n_1 groups had an energy below 1 MeV. Because in this energy range the neutron detection efficiency decreased rapidly with decreasing neutron energy, the number of neutrons counted would vary appreciably with the fluctuations in neutron energy caused, for example, by the varying energy loss of the irradiation beam in samples of different pressure and composition. In addition, because of low detection efficiency, small changes in the neutron yield might not be reflected in the observed neutron count. For these reasons, the n_1 neutron group from oxygen-16 was not suitable for measurement, and hence the n_0 group was used.

Nitrogen-14 generated seven neutron groups. The spectrum shows that the neutron group pairs (n_1, n_2) and (n_4, n_5) were not resolvable under the conditions of measurement, but this did not detract from their potential use as a measure of nitrogen content. However, the n_1 and n_2 groups had energies comparable with the energy of neutrons from carbon-12, the n_4 and n_5 groups had energies similar to those of the n_0 neutrons from oxygen-16, and the groups n_6 and n_7 had energies near to the range of rapidly decreasing detector efficiency. Consequently the n_0 and n_3 groups were used for determining the nitrogen content of a sample.

Calibration

The integrated count from a characteristic neutron group is proportional to the pressure of the gas, and its variation with pressure served as a calibration curve for the determination of the nuclide concerned. The calibration curves for nitrogen (using N_2) and carbon (using CH_4) remained linear up to pressures of 100 mm, despite the fact that the energy loss of the beam in a 3-cm sample was already significant above 50 mm. This is probably due to the fact that the reaction cross section varies little with deuteron energy in that range.

The oxygen-16 calibration curves obtained from measurements on carbon dioxide and oxygen are given in Fig. 2. The two curves (drawn as solid lines in Fig. 2) coincide and remain linear up to pressures of about 25 mm, but deviation from linearity occurs at higher pressures. The $^{16}O(n_0)$ neutrons had an observed energy of 1.039 MeV. At this energy there is an appreciable change in detector efficiency with decreasing neutron energy, but when correction is made for the efficiency loss, the calibration curve still deviates from linearity as shown dashed in Fig. 2. It can thus be deduced that the effective cross section for the reaction $^{16}O(d, n_0)^{17}F$ decreases with decreasing deuteron beam energy near 3 MeV. This conclusion is compatible with the fact that the values for carbon dioxide lie below

those obtained from oxygen because the energy loss of the beam in the former is greater.

It thus follows that when carbon and nitrogen are to be determined in thermally stable gas mixtures, analysis may be performed at any pressure over the range studied. If oxygen is also to be determined, the gas sample should be analyzed at a pressure below 20 mm. After such an analysis it may be found that an elemental component present in low concentration cannot be determined with sufficient precision. If the component is carbon or nitrogen, the analysis may be
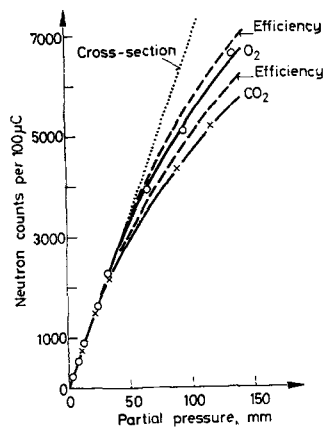

Fig. 2. Calibration curve for oxygen as measured with oxygen gas and carbon dioxide. Experimental curves (solid) are corrected for detector efficiency variation (dashed) and cross section variation (dotted)

repeated at a higher gas pressure, but if the low concentration component is oxygen, uncorrected neutron counts measured at higher pressures will lead to inaccurate results. However, the energy lost by the irradiation beam can be calculated from a knowledge of the concentrations of the major elemental components, and hence correction for variations in detector efficiency and reaction cross section can be made.

Background

The predominant feature in the background spectra (see Fig. 3) is the peak corresponding to 2.5 MeV neutrons from carbon-12 due to the residual vacuum oil vapour in the beam tube, which deposited on the hot spot generated at the point of incidence of the beam on the nickel window of the cell.

The background spectrum includes widened peaks of unknown origin. Such peaks may arise from neutrons produced by the interaction of the pulsed beam and material it strikes along the beam tube. Neutrons scattered into the detector would yield random pulses, the intensity of which would be a function of the total number of neutrons generated. In extreme cases it may be necessary to

correct for this background effect, which may be determined by irradiating a sample with approximately the same composition and pressure as the one under analysis, but in which the component to be measured is absent.
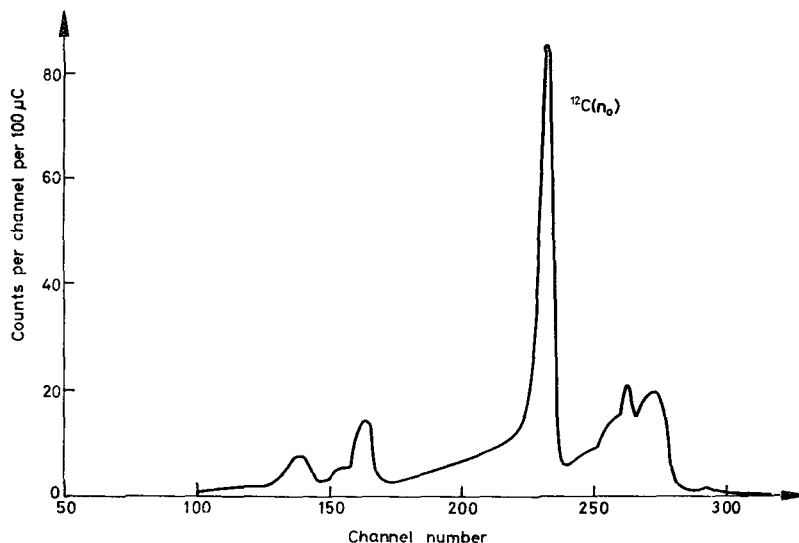

Fig. 3. Typical background spectrum. $E_d = 3.0$ MeV; $\Theta = 30°$; $s = 2.93$ m

Analyses of gas mixtures

A typical spectrum obtained from the irradiation of a CO_2/N_2 sample is given in Fig. 4. The $^{14}N(n_1, n_2)$ neutron groups have energies comparable with the energy of the $^{12}C(n_0)$ group, and the $^{14}N(n_4, n_5)$ neutron groups have energies comparable with those of $^{16}O(n_0)$ neutrons. Under constant experimental conditions, the number of counts obtained from the $^{14}N(n_1, n_2)$ and (n_4, n_5) group pairs relative to the number of $^{14}N(n_0)$ neutrons is constant and could be determined from a spectrum of nitrogen gas. From a knowledge of these ratios and the number of n_0 neutrons from nitrogen-14, the net neutron counts from $^{12}C(n_0)$ and $^{16}O(n_0)$ could be obtained.

Some typical results of elemental analyses of gas mixtures containing carbon, nitrogen and oxygen are given in Table 2, and a summary of different series of test analyses is given in Table 3. The summary includes the value of the slope of the calibration line for each test and the observed mean neutron count per mm pressure per 100 microcoulombs. In all cases the agreement between the two values was within the precision of the method. The apparent variation in the slope of the calibration curves of carbon-12 and oxygen-16 from one set of gas mixtures to the other reflects variations in the counting conditions used for the different analyses.

Table 2

Some determinations of carbon, nitrogen and oxygen in gas mixtures

Element deter- mined	E_d (MeV)	Gas mixture	Relative composition (by pressure)	Elemental concentration, (μg per cm² of beam area)			Relative error %
				Known (A)	Found (B)	Error (B−A)	$\frac{100\,(B-A)}{(A)}$
C	3.0	CO_2/CO	0.366 : 1.00	79.7	78.6	−1.1	−1.4
			1.10 : 1.00	84.9	83.2	−1.7	−2.0
			2.18 : 1.00	86.2	88.0	+1.8	+2.1
			0.365 : 1.00	188.2	187.8	−0.4	−0.2
			0.117 : 1.00	190.0	186.8	−3.2	−1.7
			0.508 : 1.00	194.4	195.5	+1.1	+0.6
N	2.0	N_2/CO_2	0.411 : 1.00	58.5	59.6	+1.1	+1.9
			19.5 : 1.00	108.0	107.5	−0.5	−0.5
			1.03 : 1.00	115.6	116.2	+0.6	+0.5
			9.16 : 1.00	166.4	163.7	−2.7	−1.6
			25.1 : 1.00	220.6	222.6	+2.0	+0.9
			40.7 : 1.00	256.3	247.8	−8.5	−3.3
O	3.0	CO_2/CO	0.117 : 1.00	109.4	108.1	−1.3	−1.2
			0.021 : 1.00	109.8	113.9	+4.1	+3.7
			0.508 : 1.00	156.7	156.5	−0.2	−0.1
			39.8 : 1.00	210.3	213.0	+2.7	+1.3
			0.366 : 1.00	318.1	319.1	+1.0	+0.3
			1.10 : 1.00	355.1	363.0	+7.9	+2.2

Table 3

Summary of test analyses on gases

$E_d = 3.0$ MeV

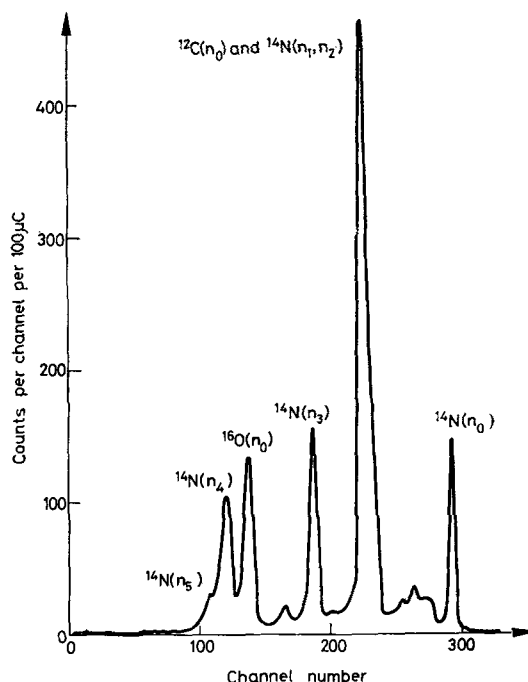| Gas mixture	Nuclide determined	Number of samples	Cali- bration*	Mean* neutron count	Mean pressure error, mm	Relative standard deviation %
CO_2/CO	^{12}C	13	179.8	174.1	+0.004	±2.3
	^{16}O	13	75.4	74.4	−0.001	±3.0
CO_2/N_2	^{12}C	9	174.3	168.9	−0.003	±2.6
	^{14}N	13	23.3	24.2	+0.004	±4.6
	^{16}O	11	68.9	69.8	−0.002	±3.4
	^{14}N	10**	23.7	23.0	−0.046	±3.3

* Counts per mm per 100 microcoulombs.
** $E_d = 2.0$ MeV

Fig. 4. Neutron time-of-flight spectrum of a mixture of carbon dioxide and nitrogen.
$E_d = 3.0$ MeV ; $\Theta = 30°$; $s = 2.93$ m ; $P_{CO_2} = 18.46$ mm; $P_{N_2} = 31.04$ mm

Precision and sensitivity

The relative standard deviation of the method was about $\pm 3\%$ for all three elements. It is satisfying to note that this precision is comparable with that of most nuclear methods used for analysis.

When nitrogen was present, the additional corrections required to obtain the net counts made a contribution to the total variance of the determinations resulting in a slightly higher relative standard deviation. The determination of nitrogen with a 2 MeV, rather than a 3 MeV, deuteron beam precluded the detection of neutrons from oxygen-16 (see Fig. 5), and resulted in a comparatively lower value of the $^{12}C(n_0)$ count, but the background continuum in the energy range corresponding to n_0 neutrons from nitrogen-14 was also lower. At the lower incident deuteron energy the $^{14}N(n_1)$ and (n_2) neutron groups were partially resolved.

Since the method requires a measurement to be made of events that are statistically random, the precision of an analysis will deteriorate as the relative statistical errors involved in determining the count rate increase. From a knowledge of the background and the slopes of the calibration lines, the minimum elemental concentration in the gas for which the neutron count can be determined with

a precision of $\pm$ 3% and $\pm$ 10% has been calculated and is given in Table 4 up to a maximum total current of 20 millicoulombs (requiring about 3 hours). When longer irradiations are practicable, the minimum quantity of these elements which can be determined without sacrificing precision, may be reduced.

The sensitivities with which the three elements that can quantitatively be detected using a charge up to 20 millicoulombs, are given in Table 5.
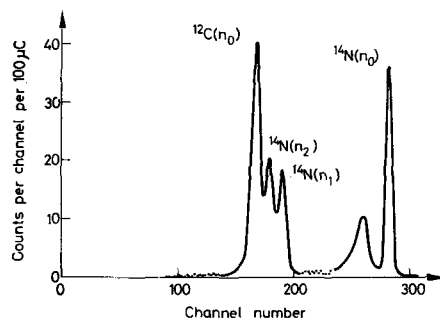

Fig. 5. Neutron time-of-flight spectrum of a mixture of carbon dioxide and nitrogen. $E_d = 2.0$ MeV; $\Theta = 30°$; $s = 2.93$ m; $P_{CO_2} = 11.66$ mm; $P_{N_2} = 19.61$ mm

Table 4

Precision limits for elemental analysis

Relative precision of neutron count	Total current, millicoulombs	Micrograms per cm² cross-sectional area of beam		
		^{12}C	^{14}N	^{16}O
$\pm$3%	1	5.18	28.40	16.79
	2	3.46	16.67	10.75
	10	1.50	5.60	4.25
	20	1.06	3.67	2.92
$\pm$10%	1	1.42	5.29	3.99
	2	0.98	3.49	2.71
	10	0.44	1.43	1.18
	20	0.31	0.99	0.82

Despite the comparatively high background in the energy region corresponding to neutrons from carbon, this element could be determined with greatest sensitivity because the reaction $^{12}C(d, n_0)^{13}N$ has a relatively high cross section. As the energies of their characteristic neutron groups were well resolved, the presence of both carbon and oxygen in the sample hardly reduced the sensitivity with which each could be determined. However, the presence of nitrogen in a sample affected the sensitivity with which the other two elements could be determined. Nevertheless, carbon and oxygen could be determined in microgram quantities with a 2 millicoulomb total current, even when the nitrogen to carbon ratio was about 2500 : 1 by weight and the nitrogen to oxygen ratio was about 75 : 1.

Table 5

Sensitivity of elemental analyses

Total current, millicoulombs	Nanograms per cm² cross-sectional area of beam		
	^{12}C	^{14}N	^{16}O
1	290	900	770
2	210	630	540
10	90	280	240
20	60	200	170

Interferences

When the sample contains other nuclides which yield neutrons with energies near to those of the neutron groups being used for analytical purposes, these nuclides would interfere with the precision of the analyses. Thus, nitrogen-14 interferes with the measurement of carbon and oxygen. Similar interference could be expected from gases containing enriched carbon-13, nitrogen-15 and oxygen-17 and 18. Even in samples in which the heavy isotopes are not enriched, neutrons generated from them may still interfere with the determination of a minor component. For example, a sample containing many carbon and only one nitrogen atom per molecule may contain carbon-13 in amounts comparable to the nitrogen content even though carbon-13 is not enriched.

If the gas under investigation contains components which decompose to form non-volatile products at high temperatures, these products could deposit at the heated point of incidence of the deuteron beam on the nickel window and at the back of the cell where high temperatures develop over small areas. The non-volatile material deposited in the path of the beam would become a source of neutrons and make accurate analysis difficult.

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