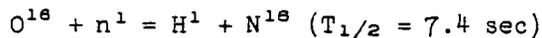


Activation Analysis of Petroleum Stocks for Nitrogen
and Oxygen by Activation with Fast Neutrons

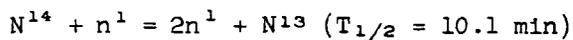
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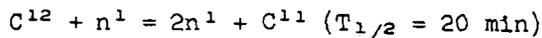
Analysis by radioactivation with neutrons from nuclear reactors is possible for most elements, in some cases with remarkable sensitivity. However, three light elements of particular interest in petroleum refining, carbon, oxygen, and nitrogen, remain quite inert under irradiation with slow neutrons. A number of metallic impurities in petroleum can be determined by activation in a nuclear reactor, but the cost of even the smallest reactor has precluded the routine application of such analyses in petroleum refining and research. In one case, a high-voltage electron accelerator, used primarily for radiation chemistry studies, has been adapted to the part-time production of a moderate neutron flux and used to advantage in routine chemical analysis,¹ but its cost is too great to justify its purchase solely for analysis. The recent availability of low-cost, low-voltage, positive-ion accelerators designed to produce neutrons has brought activation analysis within the reach of the average industrial laboratory. The neutrons formed by 150-keV deuterons impinging on a tritium target have an energy of 14 MeV. This supplies enough energy to activate oxygen by the reaction



and nitrogen by



That the energy is somewhat too small to activate carbon by the similar reaction



is fortunate from the standpoint that hydrocarbons can be analyzed for small concentrations of oxygen and nitrogen (and most of the other elements) without the hindrance of a large interfering carbon activity.

We have installed a Texas Nuclear neutron generator, Model 150-1H, and are using it for analysis of petroleum stocks for various elements by activation with the 14-MeV neutrons. At a beam current of 0.5 milliamperes on a fresh target of titanium tritide on a molybdenum disk, we find a fast neutron flux of 2×10^{10} n/sec. With the sample in a 60-ml bottle adjacent to the

target, we achieve an average flux density in the sample of 5×10^7 n/cm²-sec. In this paper, we report our experience in nitrogen and oxygen analyses.

Nitrogen Analysis

A sample up to 60 ml in a polyethylene tube or bottle is exposed to the neutron flux for 10 minutes. Then the bottle is placed in a well in a 3-inch NaI crystal for counting the scintillations produced by the annihilation photons from the N¹³ positrons. Alternatively, the irradiated sample is added to a fluorescent mixture for liquid-scintillation counting of the positrons. In either case, one to two minutes is allowed for any oxygen in the sample or container to decay. Then the nitrogen is counted for a period up to 18 minutes. The identity of the radioisotope is confirmed, when necessary, by the half-life of the decaying activity or by the pulse-height spectrum of the annihilation radiation or beta rays. We find with a flux density in a 60-ml sample of 5×10^7 n/cm²/sec, that a sample containing 1% nitrogen gives an initial counting rate of 1300 counts/sec.

Flux Monitoring

The variation in beam current and position on the target during a short irradiation or from one irradiation to another, introduces a considerable error into an analysis. The quantity of an induced activity at the end of an irradiation is

$$\int_0^T \left(\frac{dn}{dt} - \lambda n \right) dt$$

where $\frac{dn}{dt}$, the rate of production of the radioisotope, is proportional to the neutron flux. If this is constant during the irradiation, the integral has the value $\frac{1}{\lambda} \frac{dn}{dt} (1 - e^{-\lambda T})$. However, if the flux is

not constant, using the average value of $\frac{dn}{dt}$ gives only an

approximation. The final activity may deviate from the above either upward or downward, depending on whether the flux increases or decreases during the irradiation.

We have found a convenient means to monitor the flux and correct automatically for fluctuations during irradiation, as well as for errors in timing. If, during irradiation of a sample, one exposes as a monitor an object in which the neutrons will activate a radioelement of the same half-life as the activity in the sample being analyzed, the monitor will serve to automatically integrate the flux. If both the sample and the monitor are exposed in the same respective geometry in each irradiation, the ratio between the activities in the sample and the monitor will be independent of flux variations, but will vary only in proportion to the element being determined in the sample.

We have used small pieces of copper as suitable monitors for nitrogen. Copper-62, induced by the $n,2n$ reaction in copper, has a half-life of 9.8 minutes, compared to 10.1 minutes for nitrogen-13. The copper is placed in the same position in each irradiation and then counted for 1 minute, beginning 2 minutes after irradiation, in a small well counter. The count from the nitrogen between 2 and 20 minutes after irradiation is normalized to the copper count. The small difference in half-lives in this case would introduce only a 2% error in normalization if the flux changed by 20% during the irradiations.

Interferences

At nitrogen concentrations below 0.1%, several substances present in hydrocarbons may produce activities which interfere with nitrogen analysis. Atmospheric nitrogen dissolved in the sample can be as high as 0.03%; it can be purged from the sample before analysis by boiling it or bubbling oxygen through it. Copper has a high cross-section to 14-Mev neutrons for the production of Cu-62. Because it also emits positrons and has a half-life indistinguishable from that of N^{13} and because it may occur at low concentrations in petroleum stocks, it can be mistaken for nitrogen. We have been able to separate the two by pulse-height analysis of the spectra in a liquid scintillation counter using the large differences in beta-ray energies. Most important interference, however, is the nitrogen-13 activity produced in hydrocarbons by the protons recoiling from fast-neutron collisions and entering the reaction with carbon:²



We have found that this reaction produces as much N^{13} as 0.07-0.09% nitrogen in the sample, and this limits the sensitivity for detection of nitrogen in hydrocarbons to about the 0.1% level. Without this inherent interference, the sensitivity would be below 1 part per million.

Even at higher concentrations, the N^{13} contribution from this source must be evaluated to give an accurate analysis. Two samples of a lubricating oil additive compound containing 1.83% N according to chemical analysis, as well as a small amount of phosphorus, were diluted by factors of 10.7 and 8.7 in benzene and irradiated. N^{13} activities corresponding to 2.56% and 2.48% N were found. The decay of the scintillation pulses between 0.4 and 0.6 Mev fit a 10-minute curve, showing that the concentration of the phosphorus was not enough to introduce a large error. Activation of the benzene alone gave N^{13} corresponding to an apparent 680 ppm N. This contribution was subtracted to find the actual nitrogen content of the sample, 1.86%, which agrees with the chemical analysis.

Oxygen Analysis

Activation analysis has proved particularly valuable for oxygen determination since it is the only method which can give directly the total oxygen in a sample. The analysis is very rapid and subject to few interferences. The nitrogen-16 formed by the n,p

reaction decays with a 7.4-second half-life by emission of beta particles and 6 to 7-Mev gamma rays. Since these gamma rays are twice as energetic as any others encountered in activated petroleum stocks, we can eliminate interferences with a pulse-height selector set to respond only to gamma rays of greater than, say, 4 Mev.

The sample, in a 60-cc polyethylene bottle, is irradiated for 30 seconds, then transferred by pneumatic tube to a 3-inch well scintillation crystal and counted for 15 seconds. The flux monitor consists of a small piece of plastic scintillator, surrounded by lucite and attached to a photomultiplier tube. The scintillator, located a few inches from the target, detects beta particles of N^{16} produced from oxygen in the lucite. Measurement of this N^{16} activity normalizes the activity in the sample to the neutron flux used for irradiation of an oxygen standard. Since the sample and monitor are counted simultaneously, the accuracy of analysis does not depend upon precise timing of the start and duration of the counting period. Irradiation and counting of a standard and its monitor plus two or three minutes of calculation completes the analysis.

Samples which have been analyzed by this technique include polymers, lube oil additives, asphalts, and cracker feed stocks. Oxygen contents ranged from 50 ppm to 30%. Duplicate determinations agree to within 2-5%, depending on the level of activity produced. The highest sensitivity is achieved with 50-gram samples, but we have analyzed samples weighing as little as 10 milligrams. For samples containing less than 0.1% oxygen, a correction for oxygen in the polyethylene container becomes significant; and dissolved oxygen in the sample must be removed by bubbling with nitrogen. The only element interfering directly in this analysis is fluorine, which gives N^{18} via the n, α reaction. Fluorine is also activated to 29-sec O^{19} , however; and a measurement of this activity allows correction for the N^{18} contribution from fluorine.

References

- ¹ V. P. Guinn and C. D. Wagner, Anal. Chem. 32, 317 (1960)
- ² Nitrogen-13 in Hydrocarbons Irradiated with Fast Neutrons, submitted for publication in Anal. Chem.

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