Measurement of the Fluorine Content of Three NBS Standard Reference Materials by Use of the 19F(p,p'γ)19F Reaction

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MEASUREMENT OF THE FLUORINE CONTENT OF THREE NBS STANDARD REFERENCE MATERIALS BY USE OF THE ^{19}F(p, p'γ)^{19}F REACTION *

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The fluorine contents of National Bureau of Standards (NBS) Standard Reference Materials (SRM) 91, opal glass; 120b, phosphate rock; and 2671a, freeze-dried urine; have been measured using the ^{19}F(p, p'γ)^{19}F reaction at a proton energy of 3.1 MeV. The results are in good agreement with the values certified by the NBS.

1. Introduction

The analysis of fluorine (F), at trace levels, is well known to be an extremely difficult undertaking by chemical methods [1]. Its relatively low atomic number makes analysis by both X-ray and particle-induced X-ray fluorescence difficult. Neutron capture does not produce an isotope long lived enough for conventional neutron activation analysis. However, proton-induced nuclear reactions in fluorine at MeV energies have high cross sections and therefore can be used for fluorine determinations that are relatively simple and sensitive, and that require little sample preparation.

We have recently used the ^{19}F(p, p'γ)^{19}F reaction to determine trace levels of fluorine in a variety of food samples obtained from the US Food and Drug Administration and in various vegetation samples [1–3]. Comparison of the nuclear results with values obtained by use of chemical methods showed good agreement down to the 30 ppm region, but showed deviations below that level. We have also used this technique to obtain fluorine concentrations of archaeological bone samples for the purpose of determining relative dates of the samples [4]. Comparisons of the relative dates determined by the fluorine analyses to relative dates determined by an independent wet chemical technique for nitrogen showed excellent agreement. Additional applications have also been reported by other laboratories [5].

Because of the numerous applications of the nuclear method, it is important to take every opportunity to use it to determine the fluorine content of materials of known composition insofar as they exist so that the results from different methods can be intercompared. One opportunity to make such a check is furnished by the NBS Standard Reference Materials SRM 91 (opal glass), SRM 120b (phosphate rock), and SRM 2671a (freeze-dried urine). These materials have F concentrations in the few percent range and furnish an opportunity for a stringent test of the nuclear technique at relatively modest levels compared to those found for pure compounds, such as teflon or fluorides.

2. Experimental method and results

The fluorine-containing targets were bombarded with a 0.5 nA beam of 3.1 MeV protons from the Brookhaven Research Electrostatic Accelerator. The 110 and 197 keV gamma rays produced in the ^{19}F(p, p'γ)^{19}F reaction were detected with a coaxial 80 cm^3 Ge(Li) gamma-ray detector placed 4.0 cm from the target at 90° to the incident beam. The detector was 14% efficient for ^{60}Co gamma rays compared to a 7.6 cm diameter by 7.6 cm long NaI(Tl) detector. The energy resolution of the detector for the ^{19}F gamma rays was about 1.8 keV.

The samples were prepared by first shaking the powdered reference material to ensure homogeneity and then pressing the material into a disc 2.5 cm in diameter and several mm thick. The discs were then mounted in a quartz target chamber. The quartz was lined with either graphite or mylar since these materials are free of fluorine contamination and, therefore, are not a source of background when bombarded by scattered protons. A nickel foil, 2.54 μm thick, was used between the sample and accelerator vacuum systems to eliminate contamination resulting from small leaks of SF$_6$ gas from the accelerator pressure tank into the vacuum system and target chamber.
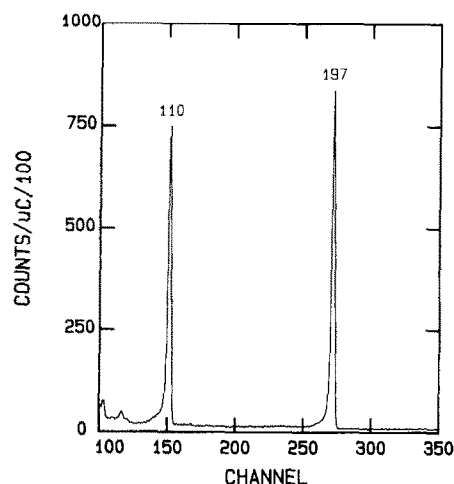
Fig. 1. Typical gamma-ray spectrum obtained from bombardment of thick phosphate rock sample with 3.1 MeV protons. The 110 ad 197 keV gamma-ray peaks from the $^{19}F(p, p'\gamma)^{19}F$ reaction are indicated.

A typical spectrum obtained from the opal glass sample is shown in fig. 1. It can be seen that the gamma rays of interest are the dominant feature and that analysis of the data is straightforward. The peaks are well defined, and peak areas can be reliably determined by summing channels in the peak and subtracting the average backgrounds determined from the channel groups just above and below the peak. The background corrections ran about 10% of the total number of events in the peak. Measurements were made on several different targets of each of the three reference materials as well as for a sample of pure teflon assumed to have the well-defined composition of CF_2.

The results in counts/μC obtained in this fashion are not in themselves sufficient to give the fluorine content of the unknowns. Since the gamma-ray produc-

tion yield is dependent on the stopping power of the matrix, corrections must be made for the target composition. These analyses were performed in the following way. The yield of gammas, N_γ, is given by:

$$N_\gamma = N_p \int_{E_0}^0 N_f(E)\, \sigma(E) dE,\tag{1}$$

where N_p is the number of incident protons, $N_F(E)$ the number of F atoms in an energy interval dE about an energy E, and $\sigma(E)$ is the gamma-ray production cross section. The number of F atoms per cm^3, N_F, can be found since $N_F(E) = N_F/(dE/dx)$ so the integral becomes:

$$N_\gamma = N_p N_F \int_0^R \sigma(E)\, dE/(dE/dx).\tag{2}$$

When results from an unknown, u, are compared to a standard, s, of similar composition, the integral is constant, and

$$\frac{N_{\gamma,u}}{N_{\gamma,s}} = \frac{N_{p,u}}{N_{p,s}} \frac{N_{F,u}}{N_{F,s}}.\tag{3}$$

However, when the standard reference material is of a different composition the integral must be included. If the stopping power is represented with a constant value S, the integral becomes [5]:

$$N_\gamma = \frac{N_p N_F}{S} \int_{E_0}^0 \sigma(E) dE.$$

In this relation the representative stopping power is determined at an energy consistent with an average value of $\sigma(E)$. The errors introduced by this are, in general, of the order of 5% or 10%. However, the errors introduced in the ratios of the yields from unknown and standard materials are negligible. It should also be pointed out that the major components of the material need to be known in order to determine the values to be used for the stopping powers. In the present experiments the compositions are taken from the NBS values

Table 1
Fluorine concentrations (in percent) of NBS standard reference materials

Material	Proton activation analysis [a]	NBS certified values	Ratio p activation analysis to NBS value
Opal glass			
SRM 91	5.70 $\pm$ 0.07	5.72 $\pm$ 0.04 [b]	0.997 $\pm$ 0.012
Phosphate rock			
SRM 120b	3.93 $\pm$ 0.09	3.84 $\pm$ 0.04 [c]	1.020 $\pm$ 0.025
Freeze-dried urine			
SRM 2671A	0.0462 $\pm$ 0.0037	0.0484 $\pm$ 0.0033 [d]	0.945 $\pm$ 0.10

[a] Proton activation analysis values are measured relative to teflon at 76 wt%.
[b] Average of determinations by five analyses.
[c] Average of determinations by six analyses.
[d] Average of 17 determinations by NBS fluoride ion selective electrode method and procedure of standard additions for quantitation.

for the major components in the SRM. Corrections for the differences in stopping powers were roughly 10% in magnitude. Cross sections as a function of E, which can be used to evaluate the integral, have been reported in refs. [1] and [3]. Since the absolute cross section data are known, the integral in eq. (2) can be performed numerically using the stopping power data of Andersen and Ziegler [6]. Performing this integration allows the determination of fluorine concentrations either absolutely, once the detector geometry and efficiency are known, or relative to a material of different composition.

The results of the measurements are shown in table 1. The proton activation values, measured relative to teflon, agree to 5% or better with the NBS certified values.

3. Conclusions

The values obtained for the fluorine content of the NBS SRMs by use of the proton activation analysis method are in excellent agreement with the NBS values which are entirely based on other more conventional methods. We have verified that the nuclear technique gives F concentrations with high accuracy and with precisions of a few percent. Thus there are no serious systematic errors at these concentration levels if variations in dE/dx of the materials are taken into account.

These conclusions are important since the nuclear method is an independent analytical tool which is quick, easy, precise, requires little or no sample preparation, and uses only minimal amounts of samples. The NBS standard reference materials contain fluorine in a useful level that is directly applicable to calibrations for trace analyses. It should be emphasized that the nuclear method does not require reference standards with concentrations comparable to the unknown; however, standards at the few percent level provide a useful bridge between compounds containing F as a major element and those containing it in trace quantities.

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