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FLUORINE DETERMINATION IN DIET SAMPLES USING CYCLIC INAA AND PIGE ANALYSIS

A. S. FAROOQI,* W. ARSHED,* O. A. AKANLE,* C. JEYNES,** N. M. SPYROU*

**Department of Physics, University of Surrey, Guildford, Surrey, GU2 5XH (UK)*
***Department of Electronic and Electrical Engineering, University of Surrey, Guildford, Surrey, GU2 5XH (UK)*

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Fluorine is an important trace element for life and human well-being. Food, in general, provides about 40 percent of the fluorine intake in the human body. In order to measure fluorine levels in human diet samples, Instrumental Neutron Activation Analysis (INAA) and Proton Induced Gamma-ray Emission (PIGE) analysis were used. Reactions $^{19}F(n, \gamma)^{20}F$ and $^{19}F(n, p)^{19}O$ were employed for determination of the fluorine concentration using a reactor neutron spectrum and epithermal neutrons. Corrections were made for the sodium matrix interference caused by the $^{23}Na(n, \alpha)^{20}F$ threshold reaction in the case of reactor neutron cyclic activation analysis and for the oxygen interference via $^{18}O(n, \gamma)^{19}O$ reaction when using the epithermal cyclic NAA method. The fluorine content of the diet samples was also determined by PIGE analysis making use of the resonance reaction $^{19}F(p, \alpha\gamma)^{16}O$ at 872 keV. Cyclic Neutron Activation Analysis (CNAA) when combined with mass fractionation was found to be the most suitable for determination of low concentration of fluorine, through the $^{19}F(n, \gamma)^{20}F$ reaction with a detection limit of 2.2 ppm in Bowen's Kale elemental standard.

Introduction

Fluorine is one of the ten elements which are considered of great importance to human health and declared as clinically essential for life[1,2]. The origin of fluorine is soil, from where it appears in water supplies, plants and animals, before finally being absorbed by human beings. Fluorine levels in drinking water have been recorded from 0.45 to 16.2ppm[2,3,4,5]. The optimum level of fluorine in drinking water supplies has been recommended as 1ppm[6]. Fluorine content of various food stuffs have been listed by the World Health Organization(WHO), showing significantly high levels of fluorine i.e., 84 to 220ppm in fresh fish, tea and baking powder[1]. Fluorine content up to 406ppm has been found in China tea[7].

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The daily intake of fluorine through food has been reported as 2.3 and 0.8mg/day in fluoridated and non-fluoridated areas, respectively, whereas through inhalation the values range between 1.4 to 3mg/day[1].

Its influence in prevention of dental caries is well- known, however, it exhibits toxic effects at elevated concentrations. There has been a growing concern in knowing the fluorine content of food stuffs[7,8,9] in order to establish intake levels in populations. This growing need for determination of the fluorine level in food requires human diet reference materials having a certified concentration of the element. The International Atomic Energy Agency(IAEA) recently launched an intercomparison programme to investigate whether three human diet specimens(F1-9, F2-9 and F3-9) were suitable reference materials as far as fluorine content is concerned.

INAA and PIGE analysis were used to obtain the concentration of fluorine in the specimens and other biological reference materials. Detection limits for the techniques were also obtained, for comparison.

Experimental Methods

The IAEA diet samples were in the form of coarse grain powder, sealed in polyethylene bags. The powder was thoroughly mixed with the help of a polyethylene spatula(but no attempt was made to homogenize the materials) before preparing pellets using a 7mm diameter pelletizer. The other reference materials IAEA Animal Bone(AB), IAEA Calcined Animal Bone(CB), Bowen's Kale(BK) and NIST Peach Leaves(P8) were prepared in a similar fashion.

Cyclic Neutron Activation Analysis(CNAA)

CNAA was employed for determining fluorine in diet samples making use of two different nuclear reactions:

(a) $^{19}F(n,\gamma)^{20}F$ ($T_{1/2}$ = 11s, E_γ = 1633keV)

(b) $^{19}F(n,p)^{19}O$ ($T_{1/2}$ = 29s, E_γ = 197keV, 1357keV).

Both reactions suffer from interferences caused by sodium and oxygen, respectively, through the following reactions:

(a′) $^{23}Na(n,\alpha)^{20}F$ and

(b′) $^{18}O(n,\gamma)^{19}O$.

Thus study of the above reactions would indicate which of the two would be more suitable to be employed in analysis, depending on the content of the interfering elements. Reaction (a) was used for the fluorine level determination using reactor neutron flux(thermal flux = 1.2×10^{12}n/cm^2/s and fast flux = 5.2×10^{11}n/cm^2/s). The interference caused by ^{23}Na was estimated by irradiating analytical grade CaF_2 and NaCl standards under the same conditions as the samples. The timing parameters optimized for fluorine measurement, with a total experimental time of about 5min, were: 10s for irradiation, 2s for decay(waiting time) and 10s for counting, repeated for 14 cycles. A single-shot(conventional) irradiation and counting experiment was also carried out to compare the detection limits for determination of fluorine with those of CNAA. The timing parameters for assessment of fluorine by single shot irradiation and counting were: 20s of irradiation, 2s of waiting and 20s for counting.

When determining fluorine through the threshold reaction (b), the oxygen interference was calculated by irradiation of analytical grade CaF_2 and MgO standards under identical conditions as the samples. In order to minimize the oxygen interference through reaction (b′) the samples were irradiated under cadmium(epithermal flux = 1.92×10^{10}n/cm^2/s). The optimum timing parameters used were: 20s of irradiation, 2s of waiting and 20s for counting, repeated for 7 cycles.

Proton Induced Gamma-ray Emission(PIGE) analysis

The target plate was prepared by sticking the pellets, using double sided adhesive tape, on a 3mm thick aluminium plate and then carbon coating, to render them electrically conducting. A pellet of IAEA Animal Bone(AB) reference material(A3-7a) was also prepared and analyzed along with the diet samples. The samples were irradiated with the proton beam from the University of Surrey's 2MeV Van de Graaff accelerator. The resonance reaction $^{19}F(p,\alpha\gamma)^{16}O$ at 872keV was thought to be the most suitable because of its large cross section(540mb)[10]. The above reaction has been used previously in fluorine determination[7,11]. A beam of about 500μm diameter was used with a nominal current of 7 to 12 nA and an incident beam energy of 880keV. The 6.13 to 7.12 MeV γ-ray signal was collected

by a 127mm diameter × 127mm NaI(Tl) detector coupled to a computer based multichannel pulse height analyser. A background spectrum was also collected with the beam falling on the beam-stop near the target chamber. The data were collected for 3μC of integrated charge, approximately of 250s duration. Rutherford backscattering(RBS), strictly speaking elastic scattering, spectra were collected simultaneously to correct for matrix effects.

Results and discussion

CNAA

The comparative method was used for determining fluorine concentration in the biological materials under study. When using the reactor neutrons, it was found for 25 replicate standards that 1mg of sodium was equivalent to 24 ± 1.2μg of fluorine through the interfering reaction $^{23}Na(n,\alpha)^{20}F$. When 25 replicate standards were irradiated under cadmium to determine fluorine concentration through measurement of ^{19}O, it was found that 1mg of oxygen was equivalent to 0.4 ± 0.1μg of fluorine.

In order to observe the accuracy of the INAA techniques employed for fluorine measurement, two IAEA reference materials, for which literature values exist, CB and AB, were first analyzed. The single shot irradiation and counting of the samples yielded detection limits of 58 and 66ppm for CB and AB, respectively, using reaction (a). This was thought to be an unsuitable technique for detection of fluorine in diet samples, since the element was expected to have lower concentrations than the detection limits obtained. Whereas when CNAA was used for the same reaction a significant improvement was found for the same materials. Table 1 lists the fluorine concentration and detection limits determined in AB, CB and the diet samples F1-9, F2-9 and F3-9.

The results obtained using reaction (b) in the analysis of CB and AB for determination of fluorine concentrations through cyclic activation under cadmium are presented in Table 2. This shows the detection limits for the element, with and without correction for the oxygen interference. These detection limits indicate that the technique is unsuitable for determining the low levels of fluorine

expected in the diet specimens (<22ppm) and indeed no fluorine was detected in the diet specimens using this reaction. The oxygen concentration in the bone reference materials and the diet specimens were estimated to be of the same order.

PIGE

The background corrected counts in the energy window, between 5.525MeV and 7.5MeV, covering the 6.13, 6.69 and 7.12MeV γ-rays were taken as the signal. Direct comparison between the signal

Table 1

Fluorine concentration (ppm) in biological materials through $^{19}F(n,\gamma)^{20}F$ reaction in CNAA.

Material	Determinations	Na/F ratio	MDL (ppm)	Present work	Reported values
AB	10	11	21	460±50	440±50[12]
CB	10	18	26	573±20	566±20[15]
BK*	5	403	2.2	6.0±1.2	5.87±0.97[16]
P8*	5	3	1.0	8.4±1.0	--
F1-9	15	370	9.4	17± 6	--
F2-9	15	260	9.5	22 ± 7	--
F3-9	15	393	9.6	17 ± 6	--

* Concentrations determined by combining mass fractionation and CNAA.

Table 2

Fluorine concentration (ppm) in reference materials through reaction $^{19}F(n,p)^{19}O$ in CNAA.

Materials	Sample mass (mg)	MDL (uncorrected)	MDL (corrected)	Fluorine content
AB	115	65	84	483 ± 37
CB	100	74	90	546 ± 41

from the IAEA Animal Bone (AB) and the diet samples was made in order to calculate the fluorine concentration. The fluorine concentration in AB was taken as 440 ± 50 μg/g[12]. The minimum

detectable level(MDL) under the experimental conditions was determined as 15μg/g of fluorine. An overall precision for determination of fluorine concentration in the diet samples was estimated as 56% whereas in the IAEA Animal Bone standard it was 6%, based on counting statistics. The results for fluorine content in the diet samples F1-9 and F2-9 are given in Table 3, quoting values with standard deviation for five determinations. Apparently PIGE does not seem promising for fluorine determination at low levels of concentration in biological samples. However, the poor detection limits and experimental precision are due to a low overall integrated charge. It is thought that longer irradiation(higher integrated charge) would lead to better detection limits since these are inversely proportional to the square root of the collected charge. An MDL of 0.96ppm for 1000μC of integrated charge has been quoted in the literature[14]. This is unreasonable for our system representing about 27 hours of irradiation at 10nA beam current and will obviously destroy the samples. A more 'reasonable' collected charge of 30μC may yield a detection limit of about 5μg/g.

Table 3

Fluorine concentrations(ppm) in human diet specimens(F1-9, F2-9) using PIGE analysis.

Diet specimen	Fluorine concentration	MDL
F1-9	21.3 ± 5	15
F2-9	17.2 ± 4.3	15

Mass fractionation

Relatively high errors(30-35%) were observed for the diet samples as compared with AB(10.8%) and CB(3.5%). The higher standard deviation associated with the diet samples may be related to the lack of homogeneity which results in high sampling factors as determined in previous work[13]. The representative mass evaluated on the basis of sampling factors for determining fluorine in the diet samples were 2 to 3g, K_1 value, in order to achieve 1% standard deviation on the results. These representative masses for

the diet samples may introduce dead times of about 100% when using the present irradiation and counting conditions. The representative mass related to K_s values, i.e. 5% standard deviation, will be reduced by a factor of 25 but at the expense of higher errors on fluorine determination[13]. The idea of mass fractionation in conjunction with CNAA using reaction (a) was therefore explored. This was shown to be useful not only in minimizing the dead time problem but also in improving the detection limits. Due to the limited amount of the diet samples supplied by IAEA, mass fractionation was carried out for the reference material Bowen's Kale(BK) and NIST Peach Leaves(P8) for which we had larger amounts. 450mg of each material(BK & P8) was fractionated into 15 subsamples of equal mass and were irradiated and counted under the same conditions. Individual spectra of 15 subsamples were added up together to achieve a cumulative spectrum and fluorine concentration was determined through reaction (a). Fluorine concentration in P8 was determined as 8 ± 2ppm while in BK it was 6 ± 1.2ppm with detection limits of 1ppm and 2.3ppm respectively. Therefore on the basis of the present work CNAA in employing mass fractionation using reaction (a) may be the best choice for measuring low levels of fluorine.

In the case of PIGE, mass fractionation will involve the addition of the individual spectra from different areas on the target sample to produce a composite spectrum representing a single long irradiation which should prove useful in improving both MDL and precision.

Conclusion

This study demonstrates that the nuclear-based techniques, INAA and PIGE analysis may successfully be applied for determination of fluorine content in biological materials. A significant improvement in detection limits and precision may be achieved by employing CNAA. However, CNAA does not provide sufficiently low detection limits for determining low levels(<10ppm) of fluorine in biological materials of the type analysed in this work. A further improvement in detection limit and precision may be achieved when combining mass fractionation with CNAA; in the present work a detection limit down to 1ppm in NIST

Peach Leaves was obtained. Mass fractionation can also be applied in PIGE analysis which may prove useful in improving detection limit and precision.

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