Nuclear Instruments and Methods in Physics Research B 342 (2015) 82–86

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

Nondestructive assay of fluorine in geological and other materials by instrumental photon activation analysis with a microtron

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ARTICLE INFO

Article history:
Received 21 February 2013
Received in revised form 1 September 2014
Accepted 16 September 2014
Available online 1 October 2014

Keywords:
Fluorine
Instrumental photon activation analysis
IPAA
Coal

ABSTRACT

Reliable determination of low concentrations of fluorine in geological and coal samples is difficult. It usually requires tedious decomposition and dissolution of the sample followed by chemical conversion of fluorine into its anionic form. The present paper examines possibilities of non-destructive determination of fluorine, mainly in minerals, rocks and coal, by instrumental photon activation analysis (IPAA) using the MT-25 microtron. The fluorine assay consists of counting the positron–electron annihilation line of ^{18}F at 511 keV, which is a product of the photonuclear reaction ^{19}F(γ,n)^{18}F and a pure positron emitter. The assay is complicated by the simultaneous formation of other positron emitters. The main contributors to interference in geological samples are from ^{45}Ti and ^{34m}Cl, whereas those from ^{44}Sc and ^{89}Zr are minor. Optimizing beam energy and irradiation-decay-counting times, together with using interfering element calibration standards, allowed reliable IPAA determination of fluorine in selected USGS and CRPG geochemical reference materials, NIST coal reference materials, and NIST RM 8414 Bovine Muscle. In agreement with the published data obtained by PIGE, the results of the F assay by IPAA have revealed erroneous reference values provided for the NIST reference materials SRM 1632 Bituminous Coal and RM 8414 Bovine Muscle. The detection limits in rock and coal samples are in the range of 10–100 μg g^{-1}.

1. Introduction

Fluorine (F) is released into the environment from several anthropogenic sources, mainly coal combustion and pyrolysis, aluminum smelting processes, production and use of phosphate fertilizers, production and use of HF from fluorite, and, despite ongoing restrictions, the use of freons. In trace amounts, F is essential for plants and animals but is toxic in excess. For humans, F toxicity is connected with a range of clinical symptoms affecting mainly dental and skeletal tissues, and denoted as fluorosis. The value recommended by World Health Organization (WHO) for maximum F content in drinking water is 1.5 mg L^{-1}, at a threshold for the negative effects in the form of mild dental fluorosis but quite close to the concentrations achieved by fluoridation of drinking water to prevent tooth decay (0.5–1.0 mg L^{-1}). Much higher F concentration in drinking water can cause the more serious skeletal form of fluorosis, which is endemic mainly in China, India, and South Africa. In Southeast China, endemic fluorosis is connected with combustion of coal in local open fireplaces, and in some provinces of China including Tibet, with drinking brick tea [1–5]. Fluorine is one of the most abundant trace elements in coal, with contents ranging from tens to thousands μg g^{-1} and an average value 80–150 μg g^{-1}. It is mostly associated with minerals, and rarely with organic matter [4–7]. Fluorine from coal combustion is released into the air as the gases HF, SiF$_4$ and CF$_4$ [3,8].

Reliable determination of F in geological samples including coal, usually in minor and trace amounts, is difficult. The standard methods of F assay as spectrophotometry, potentiometry with an ion-selective electrode, and ion chromatography, require decomposition and chemical treatment of the sample to transform F into its anionic form, commonly using distillation, alkaline fusion, combustion in a bomb, or pyrohydrolysis. These methods are tedious, which complicates their use in analyses of a large sample series, and the assay is threatened by incomplete release or loss of F from the sample and contamination of the sample by F from chemicals and vessels [7,9].

Nuclear analytical techniques have a great potential for the non-destructive assay of F in various matrices. Possibilities of neutron activation analysis (NAA), proton induced gamma-ray emission (PIGE), and photon activation analysis (PAA) for F assay

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http://dx.doi.org/10.1016/j.nimb.2014.09.023
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in biological and environmental reference materials have been compared in terms of detection limits, nuclear and other interferences [2]. PIGE was the most favoured method because of its interference-free character, allowing non-destructive determination of F at a $\mu g\,g^{-1}$ level. However, due to low penetration of protons, PIGE is limited to surface assay and its use for bulk analysis requires perfect sample homogeneity [9]. Detection limits of the F assay using the non-destructive instrumental mode of NAA (INAA) with short time irradiation were higher by at least an order of magnitude due to interference reactions on the elements Na and O. Due to the overlaying radiation of ^{28}Al, the assay is virtually impossible in geological samples.

Photon activation analysis (PAA), also called gamma activation analysis, mainly in Russian literature, is a useful complementary method to neutron activation analysis (NAA). Unlike NAA, which is based mainly on neutron capture reactions (n, γ), PAA is based on various types of photonuclear reactions according to the energy of incident gamma quanta. These reactions exhibit an energy threshold below which they do not take place. This is important for selecting the optimal beam energy for instrumental PAA (IPAA) as it allows partial suppression of interfering nuclear reactions. Thus, particularly in the analysis of geological samples, such a suppression of the matrix effects facilitates trace element determination. The higher penetration of high energy photons, and lower activities produced, also allow analysis of larger, more representative samples [10,11].

Within the photon energy range of 10–25 MeV, the (γ, n) reaction is the predominant photonuclear reaction. The reaction $^{19}F(\gamma,n)^{18}F$ has a relatively low threshold energy that favors its analytical utilization in the PAA assay of F. The reaction product, ^{18}F, is a pure positron emitter whose nuclear transformation is accompanied solely by emission of nonspecific gamma radiation with an energy of 511 keV resulting from positron–electron annihilation. Depending on the irradiation energy and sample compositions, formation of other positron emitters can interfere with the ^{18}F signal (see Table 1). For this reason, PAA has often been used combined with radiochemical separation (RPAA), e.g., for F assay of stone meteorites [14], seawater, marine aerosols and rainwater [15,16], and biological samples [2,17,18].

The application of IPAA in the F assay utilizes the possibility of suppressing or correcting for the effects of interfering photonuclear reactions. Large differences in the threshold energies of photonuclear reactions, and in half-lives of their products, allow for suppressing of the production of interfering radionuclides by optimizing irradiation energy and irradiation-decay-counting times. The major interfering pure positron emitters are either produced at significantly higher threshold energies (^{15}O, ^{11}C), or have much shorter half-lives (^{26m}Al, ^{30}P) than ^{18}F, thus they are not produced at lower beam energy, or these short-lived nuclides will decay almost completely before the ^{18}F counting starts. It is also possible to construct the composite decay curve of the 511-keV line from multiple countings and to resolve the individual components. Some other interfering radionuclides have other specific gamma lines, which allow for analyzing their contribution to the 511-kev spectral line besides the contribution from ^{18}F decay. Determining F content through the technique of IPAA has wide-ranging applications, namely: simultaneous F and P determination in phosphorites [19], F assays in pharmaceutical products, fluorapatite, vanadium concentrate from bauxite ore [20], enamels containing Ti [21], and determination of F in bones [22], in conjunction with N and P assay [23].

We tested and optimized an IPAA procedure for F assay by analysis of selected geochemical and coal reference materials with certified values of F content, and applied this to the assay of F in coal mined in the Czech Republic [24]. With respect to the contribution of F in coal to environmental pollution, development of a reliable, fast, and inexpensive instrumental method for F assay is of a great interest. The work detailed in this paper is focused on optimizing the IPAA procedure for assays of F in analysis of other materials, mostly rocks and minerals.

2. Experimental

Powdered samples (~1.5 g) were mixed with ~1 g of starch (Riedel-de Haën, soluble, Analytical Reagent), pelletized, with the pill-shaped pellet having a diameter of 27 mm and thickness of 3 mm, and heat sealed into disk-shaped capsules made of acid-cleaned, high-purity polyethylene foil. A set of single element calibration standards (calibrators for F and the interfering elements listed in Table 1) was prepared similarly as samples using 10–80 mg of element of interest in stoichiometrically defined compounds (LiF, KCl, Ti, Sc, Zr, and As oxides, Na and Ni carbonates, and Rb sulfate) of purified or higher grade, with assay ⩾98%. Copper foils were placed between each two samples to monitor the integrated photon dose.

Photon (bremsstrahlung) irradiation was carried out in the MT-25 microtron of the Nuclear Physics Institute. Samples, calibrators, and monitors were irradiated in a plastic cylindrical vessel centered on the beam axis with the sample being placed 5–11 cm downstream of the tungsten converter. In the effort towards finding the optimal procedure, samples were irradiated for 4 h at four different beam energies (15, 16, 17, and 18 MeV; the endpoint of the 1/k-bremsstrahlung energy spectrum corresponds to the electron beam energy incident on the converter).

Table 1
Parameters of photonuclear reactions considered in the fluorine assay by IPAA (data taken from [12,13]).

Reaction	Produced radionuclide	Half-life	Main photons (keV)	E_{thr}[a] (MeV)	E_{max}[b] (MeV)	σ_{max}[c] (mb)
$^{19}F(\gamma,n)^{18}F$	^{18}F	1.83 h	511	10.43	12.26	3.7
$^{35}Cl(\gamma,n)^{34m}Cl$	^{34m}Cl	32.2 m	511; 146.4	12.65	20.0	14.0
$^{23}Na(\gamma,n)^{22}Na$	^{22}Na	2.6 r	511; 1274.5	12.42	25.2[d]	12.9[d]
$^{45}Sc(\gamma,n)^{44}Sc$	^{44}Sc	3.93 h	511; 1157	11.32	19.44	39.4
$^{46}Ti(\gamma,n)^{45}Ti$	^{45}Ti	3.08 h	511; 719.6	13.19	15.8	24.13
$^{48}Ti(\gamma,p)^{47}Sc$[e]	^{47}Sc	3.3 d	159.4	11.45	n.a.[f]	n.a.[f]
$^{58}Ni(\gamma,n)^{57}Ni$	^{57}Ni	1.5 d	511; 1377.6	12.22	17.29	26.7
$^{75}As(\gamma,n)^{74}As$	^{74}As	17.8 d	511; 595.9	10.24	16.2[d]	108.5[d]
$^{85}Rb(\gamma,n)^{84}Rb$	^{84}Rb	32.9 d	511; 881.7	10.48	16. 8	194.0
$^{90}Zr(\gamma,n)^{89}Zr$	^{89}Zr	3.27 d	511; 909.1	11.97	16.7[d]	197.5[d]

[a] Threshold energy.

[b] Peak energy (at the first cross section maximum, if more peaks are present).

[c] Peak cross section (1 mb = 10^{-31} m^2).

[d] Averaged from two published values.

[e] Auxiliary reaction to evaluate ^{45}Ti interference.

[f] Not available.