Strontium Evaluation in Fodder

ION IOVITZ POPESCU[1], MARCEL DOBRE[2], RUDOLF E. NISTOR[2], N. IONESCU-PALLAS[3], SĂNDICA GRIGORA[a 4], CARMEN DOBRE[2]

[1] Member of the Romanian Academy, 125 Calea Victoriei, 010071, Bucharest, Romania

[2] Physics Department, Politehnica University, 313 Splaiul Independenţei, 060042, Bucharest, Romania

[3] National Institute for Lasers, Plasmas and Radiation Physics, PO Box MG7, 76900, Magurele, Romania

[4] Research and Development Institute for Bovine, Bucureºti -Ploieºti Street; km. 21, Baloteºti, Romania

In the present paper we compare two methods, the PIXE method and the flame spectroscopy method, for evaluation of strontium in hay, alfalfa and compost fodder. The results indicate a good agreement – fewer than 5% - between the methods used in sample evaluation.

Keywords: Strontium, fodder, PIXE, flame spectroscopy

It is a matter of current understanding that the control of food quality represents an activity of maximal importance for the human society. The more a continuous increase of the polluting factors entering the human body one records, the more this problem becomes acute. Above all these factors, the radio-nuclides of instable isotopes reveal as the most risky by their hidden nature. Actually, the nuclear pollution is responsible for most genetic mutations, for malformations of human fetus, and even for cancer. The nuclear experiments performed during the second half of the last century, as well as the nuclear accidents, among the best known is that of Chernobyl, are responsible for the fallout in the environment of a large number of radio-nuclides [1]. The aggravating factor consists in the uncontrolled dispersion by atmospheric winds of the products generated by nuclear activities, up to great distances from their production location. These radioactive products will gradually settle down to the earth's surface, thus entering the vegetal and animal circuits, and finally leading to the contamination of the food chain.

The alkali earth metal strontium has four stable, naturally occurring isotopes: ^{84}Sr (0.56%), ^{86}Sr (9.86%), ^{87}Sr (7.0%) and ^{88}Sr (82.58%). Sixteen unstable isotopes are known to exist. The half-life time of the ^{80}Sr, ^{81}Sr and ^{91}Sr isotopes is smaller than 3h, while that of ^{82}Sr, ^{83}Sr, ^{85}Sr and ^{89}Sr is smaller than 65d [2] Of greatest importance is ^{90}Sr with a half-life of 28.78 years. It is a by-product of nuclear fission which is found in nuclear fallout and presents a health problem since it substitutes for calcium in bones, preventing expulsion from the body. This isotope is one of the best long-lived high-energy beta emitters known.

After the Chernobyl accident all children have been affected by the long life ^{90}Sr [3]. The measurements performed on various population groups demonstrated that the population infestation with 90Sr on the earth surface is not uniform, the most affected being the temperate zones. However, food habits could heavily contribute to the infestation of the human body. Thus, although in the extreme North the ^{90}Sr air pollution represents at least an order of magnitude lower than that in the temperate zones, the massive lichen consumption, due to their ^{90}Sr capture from the air, leads to the highest ^{90}Sr concentration in the bones of the population living in these zones [4].

Generally, Strontium is capturated first in the vegetation, thus entering in the food of animals and eventually located in their bones. Animal bone contribution to human food is negligible, however, animal milk very rich in Ca is containing also the stable isotopes of Sr. Therefore, in the case of radioactive earth contamination, long half-life isotope ^{90}Sr represents the main vector contributing to the human body contamination. This is why the control of horned cattle fodder represents the only realistic preventive means against the human body contamination with ^{90}Sr.

The goal of the paper is to compare the PIXE method and the flame spectroscopy method for ^{90}Sr evaluation in fodder.

As a matter of fact, ^{90}Sr presence in the atmospheric air can occur only as a result of a nuclear accident. Therefore, currently, one monitors only the stable isotopes concentration in fodder, particularly that fodder that exhibit a high Strontium absorption, and thus containing also a corresponding high concentration. Usually, the radioactive isotope ^{90}Sr is identified by its beta radiation and/or by mass spectrometry [5]. The calculus of the effective absorbed strontium isotopes doses are given in APPENDIX.

The "Pixe" method

The word PIXE is the acronym of "Particle Induced X-ray Emission". The principle of the PIXE method consists in the extraction of the electrons from the deep energy levels, followed by the rearrangement of the electrons of the shallow levels, a process accompanied by the characteristic X-ray emission. The investigated samples are mounted as targets for the bombardment with protons, neutrons, alpha particles, or heavy ions produced by an accelerator, having energies in the range of 1-10 MeV per nucleon. The energetic particles will interact with the atomic electrons, having a good chance to extract them. The holes created in this way in the inner shells, for instance in the K-shell or L-shell, are eventually occupied by electrons of the outer shells, a rearrangement process accompanied by the corresponding energy emission as K, or L characteristic X-ray.

Generally, in a good approximation, the characteristic X-ray radiation has an isotropic distribution. Consequently, an element ${}^{A}_{Z}X$ of a thin sample will produce the counting of a number n_i of X-ray emission events in a detector, within a solid angle $\Delta\Omega$, namely [6]

$$n_i = \sigma_i^{emis} N_P \frac{t_z}{A\mu} \frac{\Delta\Omega}{4\pi} \varepsilon_d C_{abs} \quad (1)$$

* (+40) 021 402 91 02

where the emission cross section σ_i^{emis} can be written as a product of the hole production cross section σ_i^{vac} and the fluorescence yield ω_i, the latter representing the probability that the X-ray be emitted by the occupation of the hole in the *i* shell (K, L, M, etc), hence we finally have

$$\sigma_i^{emis} = \sigma_i^{vac} \cdot \omega_i \quad (2)$$

The number of incident projectile particles is N_p and $\frac{t_z}{A\mu}$ stands for the number of atoms of the element ${}^A_Z X$ per area unit, where t_z is the mass on the area unit, A the atomic mass and μ is the atomic mass unit ($\mu = 1{,}66 \times 10^{-27}$ Kg). The internal efficiency of the X-ray energy detector is denoted by ε_d and C_{abs} the absorption factor referring to the attenuation of the X-rays along their path from the sample up to the detector, passing through windows, air, external absorbers, and perhaps a short distance within the sample.

For each electronic shell, the characteristic X-rays bear its name, for instance the transitions to the K-shell give rise to the K_α and K_β radiations and the transitions to the L-shell to the L_α, L_β, and L_γ radiations. Generally, Eq. (1) holds true for each shell separately, with its own emission probability. Therefore, the overall emission cross section of a given shell is the sum of the cross sections given by Eq. (1) for each X-ray component corresponding to that shell, computed with the help of its own parameters dependent of energy, such as ε_d and c_{abs} .

The theoretical values of the emission cross sections for the K-shell, σ_i^{emis}, can be obtained by using the Born approximation, as described by Merzbacher and Lewis [7]. Inasmuch as the PIXE analysed samples are usually made up of complex chemical substances, having a great number of atoms, each atomic species will emit its own characteristic radiation. Consequently, the detector will record a compound spectrum, a sequence of X-ray maxima at various energies, each maximum corresponding to a given chemical element. The detection of the characteristic X-ray radiation has been performed with Si and Ge detectors and a typical PIXE spectrum is shown in figure 1. As one may notice, the recorded emission spectrum contains informations about a great number of chemical elements constituting the sample.

For the sake of energy calibration and correlation between maxima and their corresponding chemical elements, one makes use of the so called marker. That means a deliberate introduction besides the analyzed sample of a chemical element, whose characteristic X-ray emission induced by particle bombardment is known with precision. In the case of our samples, an Y internal marker has been used, and this is distinctly indicated in the spectrogram. These spectral maxima represent a direct measure of the relative concentration of the various elements of the sample and of the marker. One can reach in this way to evaluate concentrations as low as one part per billion (ppm).

There are many causes generating errors in a spectrogram evaluation. These are related to the statistical methods involved in spectrogram evaluation, to the radiation background, to the secondary fluorescence, to X-ray self-absorption by sample and by filters [8]. In spite of those different possible errors, their sum does not usually exceed 5%, even in the case of thick samples (when the incident particle beam becomes gradually attenuated by the first layers of the penetrated target). In the latter case, it may happen that we are not able to know the exact value of the X-ray beam energy lost in its path across the sample.

The PIXE method has many advantages. The only major inconvenience is the particle source, that is either a nuclear reactor, or a particle accelerator, that is big installations, working at high costs. However, the advantages are not at all negligible and are listed below:

The method is non-destructive. This advantage is not evident for fodder, but in cases of unique or minute samples the PIXE advantage becomes crucial.

The small evaluation time, of about 15 min.

The samples do not imply any special processing. In our case, we had to perform only simple pressings, dryings, and calcinations, but there are cases when even such processing was not necessary. Specific for our fodder samples was the necessity of the water elimination in order to increase the volume concentration of the analyzable.

For most of the chemical elements with an order number of $Z > 13$, the sensitivity is of the order of parts per billion, or even less. The PIXE method is ideal in the case of the identification of trace elements.

The needed devices for PIXE spectra detection, recording, and data acquisition and processing is currently available, such as Si or Ge semiconductor detectors, coupled to standard electronic devices, a multi-channel analyzer, and a computer.

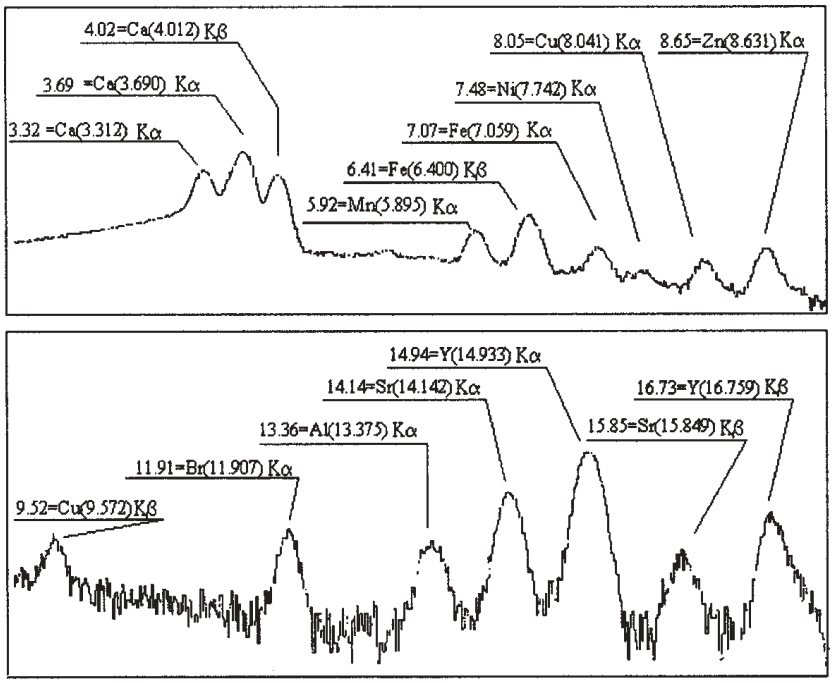


Fig.1. Typical X ray probe detected signal. Y is the internal marker

Table 1
STRONTIUM CONCENTRATION OF 12 DRY MASS SAMPLES OF FODDER DETERMINED BY SPECTROSCOPIC AND PIXE METHODS

SAMPLE	Sr (%) mass x 10^{-3} SPECTROSCOPIC METHOD	Sr (%) mass x 10^{-3} PIXE METHOD	Relative Error in %
Hay sample1	5.44	5.28	-2.94
Hay sample2	9.29	9.06	-2.47
Hay sample3	9.88	10.12	+2.43
Hay sample4	3.29	3.22	-2.13
Alfalfa sample1	3.71	3.66	-1.35
Alfalfa sample2	5.50	5.55	+0.91
Alfalfa sample3	2.48	2.41	-2.82
Alfalfa sample4	2.26	2.25	-0.44
Compost footer sample1	7.03	6.98	-0.71
Compost footer sample2	5.44	5.43	-0.18
Compost footer sample3	6.09	6.16	+1.15
Compost footer sample4	7.11	7.35	+3.38

The flame spectroscopy method

Generally, the flame spectroscopy, that is the spectrochemical analysis of the flame, is used for the determination of metallic elements but also of the elements of organic molecules. The flame spectroscopy is the most sensitive method of chemical analysis amongst all known analytical methods. A few milligrams of sample is usually sufficient for the identification of an element in a sample in a per cent of a few parts per million. Moreover, the various atomic species of the sample can be simultaneously detected, thus without any need of preliminary steps of chemical separation.

Let us summarize the advantages of the flame spectroscopy method:

The measurement occurs instantaneously, so as the flame oxidation process is. This advantage is important when one analyses toxic substances.

All detectable elements of a sample are evidenced with the same sensitivity, that of used method.

There is no so called toxicity memory effect. Even if a high concentration toxic element has been identified, after a few seconds only one can continue the identification with the same precision of any other chemical element.

A low noise spectral analysis in the ultraviolet wavelength range can be performed with a hydrogen flame, by simply burning the hydrogen in the air.

All elements of a sample can be identified simultaneously. This is possible because the spectral lines of the various chemical elements are distinct.

Sample processing

Because the samples (fodder and evaporated milk) easily undergo biological modifications (mould), leading to increase or to loss of the apparent mass, we had carefully visually pre-inspected each sample.

The samples were mechanically homogenized, partitioned in aliquots of 1.5 g each, and stored in cool air tight bags.

Sample processing for spectroscopic analysis

a1. The fodder samples have been maintained for one hour in a drying oven (at 105 °C), then determined their weight and continuing their drying for another half an hour, when stating the steadiness their weight. The fodder processed in this way has been partitioned in samples of 0,5 g +/- 0.00002 g each..

a2. The samples have been mineralized by the Kejdhal method and microwave heating.

a3. After cooling, the cartridges containing the mineralized samples were open and maintained inside the oven in order to ventilate the nitrogen oxides. Finally, the cartridge content has been diluted with 5 mL of distilled water and analytically transferred into marked balloons of 50 mL each.

Sample processing for PIXE analysis

b1.After the visual inspection, mechanical homogenization and water contents evaluation, the samples were calcinated and the resulting ashes were pressed and encapsulated.

b2.The samples processed as described, were subjected to proton bombardment from the tandem accelerator at IFA – Magurele (Romania)

Results comparation

The samples originate from fodder of hay, alfalfa, and compost. In order to compare the results obtained by both flame emission spectroscopy and PIXE, the values of Strontium concentration were always reported to the initial mass of the originating substances, notwithstanding their subsequent processing. The mass Strontium concentration of 12 dry mass samples of fodder, measured by spectroscopic and PIXE methods, are given in table 1.

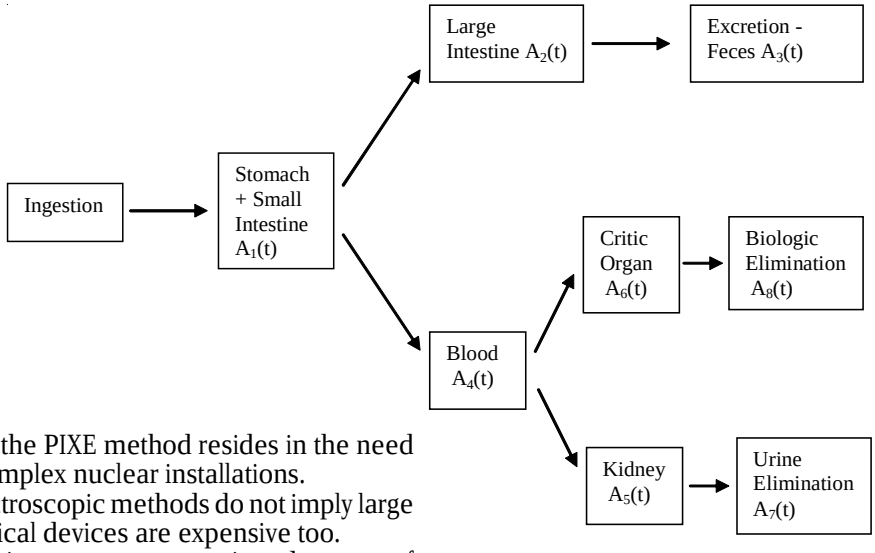
Conclusions

As a conclusion of our measurements, performed by two different analytical methods, we can summarize as follows:

Both methods allow current evaluations of Strontium concentrations down to a level of parts per billion.

The measurement errors can be reduced up to about 5%.

The PIXE method is more rapid, avoiding preliminary sample processing, such as in the flame in spectroscopic methods.



A shortcoming of the PIXE method resides in the need of expensive and complex nuclear installations.

Although the spectroscopic methods do not imply large installations, the optical devices are expensive too.

The analysis duration represents a major advantage of the PIXE method (about 15 min per sample). Taking into account that milk is a perishable product, the factor time is decisive. Consequently, the PIXE method is highly preferable, even in cases when the samples have to be transported over long distances between the production farm and the nuclear facility.

The methods presented above can be used for examination in judicial litigation cases with dangerous products.

Appedix

Let us assume the following scheme regarding the biochemical assimilation processes of the ingested soluble radioactive substances [9].

In the case of a single ingestion, we can write:

$$A_1(t) = A_0 e^{-\frac{t}{T_f}}\left[k_e e^{-\frac{t}{T_g}} + (1-k_e)e^{-\frac{t}{T_d}}\right]$$

$$A_2(t) = A_0 k_e e^{-\frac{t}{T_f}}\left(1-e^{-\frac{t}{T_g}}\right)e^{-\frac{t}{T_e}}$$

$$A_3(t) = A_0 k_e e^{-\frac{t}{T_f}}\left(1-e^{-\frac{t}{T_g}}\right)\left(1-e^{-\frac{t}{T_e}}\right)$$

$$A_4(t) = A_0(1-k_e)e^{-\frac{t}{T_f}}\left(1-e^{-\frac{t}{T_d}}\right)\left[k_R e^{-\frac{t}{T_{t,o}}} - (1-k_R)e^{-\frac{t}{T_{t,r}}}\right]$$

$$A_5(t) = A_0(1-k_e)(1-k_R)e^{-\frac{t}{T_f}}\left(1-e^{-\frac{t}{T_d}}\right)\left(1-e^{-\frac{t}{T_{t,r}}}\right)e^{-\frac{t}{T_{b,r}}}$$

$$A_6(t) = A_0(1-k_e)k_R e^{-\frac{t}{T_f}}\left(1-e^{-\frac{t}{T_d}}\right)\left(1-e^{-\frac{t}{T_{t,o}}}\right)e^{-\frac{t}{T_{b,o}}}$$

$$A_7(t) = A_0(1-k_e)(1-k_R)e^{-\frac{t}{T_f}}\left(1-e^{-\frac{t}{T_d}}\right)\left(1-e^{-\frac{t}{T_{t,r}}}\right)\left(1-e^{-\frac{t}{T_{b,r}}}\right)$$

$$A_8(t) = A_0(1-k_e)k_R e^{-\frac{t}{T_f}}\left(1-e^{-\frac{t}{T_d}}\right)\left(1-e^{-\frac{t}{T_{t,o}}}\right)\left(1-e^{-\frac{t}{T_{b,o}}}\right) \quad (A1)$$

The notations of Eq. (A1) have the following meaning:

A_0 - Activity of ingested food,

$A_1(t)$ - Activity in the stomach and in the small intestine,

$A_2(t)$ - Activity in the large intestine,

$A_3(t)$ - Activity excreted by feces,

$A_4(t)$ - Activity in the blood,

$A_5(t)$ - Activity in the kidneys,

$A_6(t)$ - Activity in the critical organ, under the assumption that the radioactivity cumulates primarily in a single organ,

$A_7(t)$ - Activity eliminated by urine,

$A_8(t)$ - Activity eliminated by unspecified biological processes within the critical organ,

k_e – Activity fraction passing in the large intestine,

k_R – Activity fraction passing in the critical organ,

T_f – Radioisotope mean life time,

T_g – Mean biological transit time to the large intestine,

T_d – Mean biological digestion time,

T_e – Mean biological feces excretion time,

$T_{t,o}$ – Mean biological transit time to the critical organ,

$T_{t,r}$ – Mean biological transit time to the kidneys,

$T_{b,o}$ – Mean biological elimination time out of the critical organ,

$T_{b,r}$ – Mean biological elimination time out of the kidneys.

Excepting T_f, the rest of the seven times characterize each chemical element containing the radionuclide. In addition, we have the relationship

$$\sum_{k=1}^{8} A_k(t) = A_0 e^{-\frac{t}{T_f}} \quad (A2)$$

It is worthwhile to note that the coefficients k_e do not all vanish, though we assumed above that we will primarily consider radio isotopic soluble salts. Table 1 gives the transfer coefficients from the gastro-intestinal tract into the blood, that is the value $(1- k_e)$, for some elements of radiobiological interest [10, 11].

The total dose absorbed during the time interval $\Delta t = t_2 - t_1$ is composed of the weighted sum of the doses located

Table 2

VALUES OF $(1- k_e)$ FOR SOME HIGH INCIDENCE RADIO-NUCLIDES

Radionuclide	$(1- k_e)$%	Radionuclide	$(1- k_e)$%	Radionuclide	$(1- k_e)$%
^{131}I	100	^{35}S	56	^{185}W	10
^{137}Cs	100	^{95}Nb	45	^{210}Po	3
^{87}Rb	100	^{64}Cu	28	^{111}Ag	2
^{14}C	95	^{60}Co	20	^{140}La	0.3
^{22}Na	95	^{103}Rh	20		
^{40}K	90	^{226}Ra	15	^{103}Ru, ^{144}Ce, ^{144}Pr, ^{147}Nd, ^{147}Pm, ^{232}Th, ^{238}U	0.05
^{45}Ca	90	^{210}Pb	10		
^{55}Fe	80	^{54}Mn	10		
^{32}P	70	^{65}Zn	10		
^{90}Sr	60	^{140}Ba	10	^{239}Pu	0.01

in the various parts of the human body

$$D = N_1 \frac{m_1}{M} D_1 + N_2 \frac{m_2}{M} D_2 + N_4 \frac{m_4}{M} D_4 + N_5 \frac{m_5}{M} D_5 + N_6 \frac{m_6}{M} D_6 \quad \text{(A3)}$$

where D_j is the dose received by the organ in which is located the activity A_j, and N_j is a dimensionless coefficient taking into account the probability - different for various organs – to produce cancer, or irreversible lesion, by the absorption of the same energy per mass unit. m_j is the mass of the organ *i*, and M is the mass of the whole body.

Bibliography

1. SANDALLS, F.J., SEGAL, M.G., VICTOROVA, N., Hot Particles from Chernobyl: A review. J. Environ. Radioactivity, **18**, nr. 1, 1993, p. 5
2. *** U. S. Department of Energy, Index of Isotope Products (2005), http://www.ornl.gov/sci/isotopes/catalog.html
3. KORBLEIN A. Strontium Fallout from Chernobyl and Perinatal Mortality in Ukraine and Belarus. Radiats Biol Radioecol, 43, nr. 2, 2003, p. 197
4. GORDON E. et al. URANIUM- A Discussion Guide, section C3 (2005), http://www.ccnr.org/nfb_uranium_2.html#C.4
5. HERRMANN, A., STÖCKLI, M., ZEHRINGER, M., Investigation of Strontium-90 intake in teeth of children living near Chernobyl, Internal Report, Kant. Laboratorium, Food Control Authority, State Laboratory of Basel-City, Switzerland, 2006
6. JOHANSSON, S., A., E., CAMPBELL, J.,L., PIXE. A Novel Technique for Elemental Analysis, John Wiley and Sons, 1988
7. MERZBACHER, E., LEWIS, H., W., Handbuch der Physik**,** Springer, **34**, 1958, p. 166
8. HAVRANEK, V., .HNATOWICZ, V., J.KVITEK,OBRUSNIK,I., PIXE-INP Computer Code for PIXE Analyses of Thin and Thick Samples, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, B85, 1994, p. 637
9. IONESCU – PALLAS, N., ONCESCU, M., Some Aspects Concerning Dose and Activity Evaluation in the Case of the Accidental Radioactive Contamination in Romania during summer 1986, Internal Report, ICEFIZ RB-19-1987: 2-12, 1987
10. LUDWIG, F., Radioactive Izotope in Futter und Nahrungsmittel, Bd.7 München, 1962
11. KIEFER, H., MAUSHART, R., Radiation Protection Measurement, Pergamon Press, 1972

Manuscript received: 27.11.2006