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Determination of Aluminium in Rock Samples by Energy Dispersive Fluorescence Spectroscopy

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Optical emission spectroscopy and fast imaging of the arc process of aluminium and its alloys were carried out to determine the concentration of the aluminium in the rock samples. Optical measurement allow the establishment of relationships between the spark aspect and the aluminium emission line's intensity. The proposed method has been applied to the determination of aluminium in rock samples with satisfactory results. The simplicity, low cost and easy operation were the main advantages of the present procedure. The proposed method was applied to the simultaneous multielement determination. The results were well within the recommended standard values.

Key Words: Aluminium, Atomic fluorescence, Spectral interferences, Atomic emissions, Diffraction in UV, Dispersive fluorescence, Arc excitation spectrum, Optosensor.

INTRODUCTION

It has been known since 19th century that aluminium can be complexed by natural flavanoids and polyphenolic compounds and that this complexation may trigger fuorescence. Although aluminium is the most abundant metal in the earth's crust, it shows a low bioavailability and it is still questionable, if aluminium has biological functions. Acid rains cause partial dissolution of soil aluminium leading to an increase in the aluminium concentration in natural waters and biological systems. Recent reports associated aluminium with several skeletal (osteomalacia) and neurological disorders, (encephalopathy, Alzheimer's disease), in humans. It was suggested that exposure to aluminium might present a hazard to health. Hence, the determination of trace aluminium is very significant. At present, for the determination of aluminium, the methods employed were spectrophotometry, spectrofluorimetry and atomic absorption spectroscopy. Among them, spectrofluorimetry and dispersive fuorescence spectroscopy were more applied because of its high sensitivity and simplicity. Aluminium can be bound to 8-hydroxyquinoline and form the steady complex with fluorescence under certain experimental conditions. Nowadays, the development of fluorescence microscopy opens a new way to explore with the

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design of fluorescent probes for aluminium imaging, especially in biological media. The fluorescence spectra of Al(III)-complex in different media, (water, micelle, various microemulsions), were reported. Florescence spectra were observed in the range 425-650 nm. The fluorescence intensity and relative fluorescence quantum yields in different media were also reported[1]. Aluminium is one of the most abundant elements in the earth's crust, being thus ubiquitous in the environment. In aquatic ecosystems, elevated levels of aluminium were known to cause toxicity in fish, algea, bacteria, plants and other aquatic species. In addition, Al(III) has the potential to produce toxicity that has been most commonly seen in patients who have reduced or absent renal function because the kidney is the primary organ of aluminium elimination[2]. The continuum emission between 400-750 nm results from collision-radiative recom-bination of electrons (bound free transitions) and from Bremsstrahlung radiation (free-free transitions) was discussed. Among these emission lines, the Al one is the particular interest because it may give information about the phenomena occuring at the material surface or at the metal-oxide intreface. Indeed, as the process starts, no spark occurs and the aluminium line intensity (I_{Al}) stays at zero level. Typical emission spectrum in UV-vis. Range of the microark plasma in solution was reported. Al$^+$ at 358.7 nm, Al at 394.4 and 396.1 nm were observed. In the elements belonging to the third period, the K_α spectrum results from decays from L shell to K shell whereas the K_β spectrum is caused by decays from M shell, where the valence electrons are placed to K shell[1-12].

EXPERIMENTAL

Rock samples were taken from the mountains of north east of Black Sea side and used without any purification. The home made electoark and electrosparc systems employed. It consists of a generator "varisource", Jarrel Ash model-70 spectrograph and all other eletronic devices specially designed. The distance between carbon electrodes was 3 mm and the selected discharge times were 1-5 min. The arc system dischaged at 20 kV. Fig. 1 shows the block diagram of the experimantal set-up.

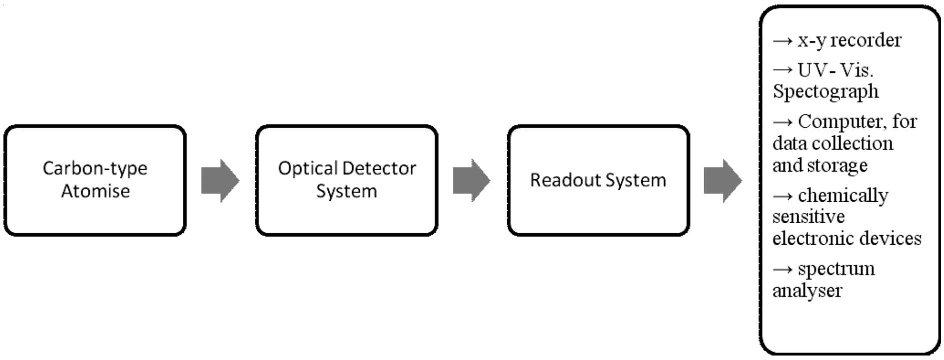

Fig. 1. Block diagram of the experimental set-up

RESULTS AND DISCUSSION

Energy dispersive fluorescence spectrometry is an anaytical technique based on the measurement of the energy and intensity of characteristic emissin from the elements present in unknown sample. Qualitative information about the sample is contained in the energy of the measured fluorescence lines from X-ray to IR, quantitative information is provided by the intensity of the emitted lines. The elements of interest in the sample are called analytes, the characteristic emitted spectrum from the elements of interest in the sample are called the analytes lines. Analytes lines are excited by shining x-rays having an energy greater than the absorption edge of the absorbed by atoms in the sample, electrons are ejected from the atoms, leaving vacancies in electron shells. These vacancies are filled, characteristic X-rays are emitted from the atoms. The energy of the characteristic X-rays or analyte lines depend on the shell of the vacancy and on the shell of the cascading electron. This process is called X-ray fluorescence. The relative intensity of the K_α-K_β depends on the probability of the vacancy being filled by an electron from the L-shell or from the M-shell. The ratio of K_α-K_β depends only on the atomic number of the atom and therefore is always constant for a given atom. Some of the vacancies caused by the photoelectric effect are not filled by the emission of X-rays. The ratio of vacancies which are filled *via* X-ray emission to the total number of vacancies is called the fluorescence field, the fluorescence yield depends mainly on the atomic number and series of the line. When a sample is fluorescenced by any one of the excitation technique, the intensities of the analyte's lines can be measured as primary or secondary fluorescence. The measured intensity of an analyte is usually proportional to the concentration of a particular analyte. Another technique is to use an atomizer in which the rock is burned out in order to get excited atoms, it is expected to get the characteristic emission lines from all of the atoms in the rock sample as atomic fluorescence. Fig. 2 shows the atomic fluorescence lines of the atoms. If the emission spectrum of aluminium is known, we can easily recognize the emission lines of the aluminium among the other emission lines on the spectrum. After selecting the characteristic emission lines of aluminium, we measured the intensity of the emitted lines, which are proportional to the aluminium concentration in rock sample concentration.

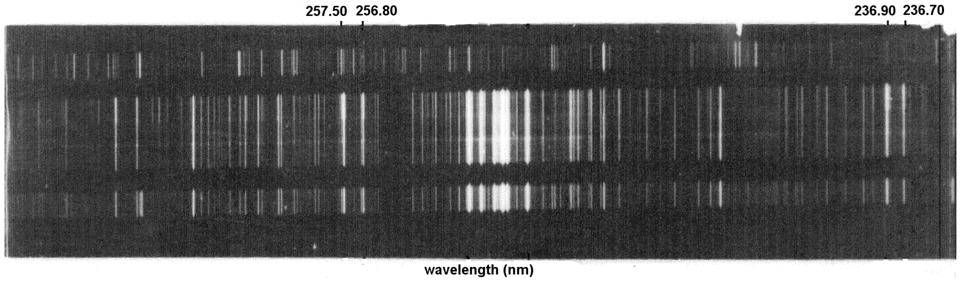

Fig. 2. Atomic fluorescence spectrum of aluminium in rock samples

When Al in the rock sample has an intense emission line which are above the absorption edge of the analyte, there is a possibility that the analyte will absorb an X-ray from the interfering element and emit an analyte line. This process is called secondary fluoresence or enhancement. When a sample is a thin film rather than a bulk sample, the secondary fluorescence is drastically more complicated for both recording techniques, therefore for secondary fluorescence, the sample thickness has to be a finite thickness. Atomic emission fluorescence spectrometry provides an accurate determination of the composition of many types of materials with little sample preparation. In some cases where no suitable standards are available, fundamental parameters can be used to provide a semi-qualitative result. Iron emission lines were used to calibrate the wavelength scale for aluminium atomic emission spectra.

Atomic fluorescence spectroscopy offers attractive analytical advantages in terms of sensitivity, selectivity, speed, simplicity and cost-effectiveness. In this paper, the feasibility for the sensitive and selective determination of "Al" in rock samples was reported. This work provides a straight-forward and cost-effective methodology for routine analysis of aluminium. The fluorescence of Al (III)-complex in different media were reported[3]. The excitation wavelength was 380 nm and the emision band, $\Delta\lambda_e$ = 425 - 650 nm, was observed in water, micele and various microemulsions. Table-1, shows the characteristics emission lines for aluminium. Most of the characteristic values were taken from the X-ray data of HNU-Co-USA. Fluorescence quantum yields of Al in solution can be measured but the fluorescence quantum yield of Al in rock cannot be measured with our recording technique because concetration of the emission spectum of aluminium is depending on the burning time.

TABLE-1
X-RAY CRITICAL ABSORPTION AND EMISSION ENERGIES
FOR ALUMINIUM, ENERGIES ARE IN keV[13]

K_{abs}	1.559
K_{α_1}	1.487
K_{α_2}	1.486
K_{β_1}	1.553
L_{Iabs}	0.087
L_{IIabs}	0.073
L_{IIIabs}	0.070

$$\phi_f = \frac{\text{Number of photons emitted}}{\text{Number of photons absorbed}} \quad (1)$$

$\lambda_{abs.}$: cannot be measured, $\lambda_{em.}$: can be measured.

Microenvironment character changes with the applied HV and burning time. Number of emission spectum of aluminium is not even during the burning time. Aluminium was shielded with the other atomic emissions because the temperature in the burning cavity is above 2500 ºC.

Fluorescence intensity is constant within the experimental error because the concentration of aluminium in every selected rock is not the same. For this reason small samples from bulk rocks were taken and mixed evenly in powder form before getting the atomic emission spectrum. The system is completely different than the aluminium in solution measurements. Using collimator on the beam did not change the fluorescence intensity, the only factor affecting the fluorescence intensity was the burning time. Changing the applied potential difference from 10-20 kV did not change the fluorescence intensity, which means all the aluminium atoms in rock was excited therefore calculation of the concentration of aluminium is more accurate than it was measured in solution. Another advantage of this recording technique is to work in a dry environment therefore Soggy components cannot be seen, which are reflecting, refracting and difracting the fuorescence beam. Another advantage of this technique is to digitize the fluorescenec lines therefore we definitely know the shape, energy, type of electronic clouds were created during the burning processes. If there are other metal atoms in the rock sample, we have a change to monitor the fluorescence emissions of the other materials. This means in one simple experiment we can record different atomic emissions. Rock samples are opac therefore Raman Scattering cannot be observed. During the atomization process of the rock sample, we can also create some of the ions, Al^+, Al^{2+}, Al^{3+} which will interfere the fluorescence lines at high temperature. Due to the atomizer molecular fluorescence cannot be seen. Therefore, all the emission spectra of aluminium are atomic in nature.

By using fluorescence spectroscopy techniques for aluminium in drinking water were measured earlier which is causing aging problem. The discharge cavity temperature during the burning process does not influence the noise, but thermal photons may induce an interference effect, at a given wavelengths in UV atomic fluorescence spectra demostrate ultra-trace analysis of metal pollutants in drinking and surface water, vegetable and fruit.

As future developments, the research will focus on improving the selectivity by developing multi-component determination in mixtures, using both laser induced fluorescence and excitation emission matrix and the temporal resolution and employing data analysis techiques like principal components regression and partial least square, which are the *in situ* reactions of the rock system. The aluminium content in the minerals which are carried with the underground water has been identified in biomedical studies as a key player in the suspected free radical oxidant-mediated pathology of human cells.

A mixture of water and small pieces of solid aluminium can create slurry sample in drinking water therefore microemulsion, which are made from contaminated polywater, an organic solvent and a surfactant and occasionally an alcohol as a cosurfactant, have unique properties as media. Partition and the interfacial adsorption of a solute in the micro-heterogeneous systems are responsible for the chemical reactivity. The sensitizing effect of microemulsion in the determination of aluminium-metal ion by spectrophotometry was determined. A non-ionic microemulsion medium by fluorescence quenching method was satisfactory but microemulsion applications to spectrofluorimetry to be lacking. Fluorescence spectra were very complex in micelle.

REFERENCES

1. X. Zhu, L. Bao, R. Guo and J. Wu, *Anal. Chim. Acta*, **523**, 43 (2004).
2. J.F.G. Reyes, P.O. Barrales and A.M. Diaz, *Talanta*, **65**, 1203 (2005).
3. J.B. Mulon, E. Destandau, V. Alain and E. Bardez, *J. Inorg. Biochem.*, **99**, 1749 (2005).
4. N. Carrion, A.M. Itriago, M.A. Alvarez and E. Eljuri, *Talanta*, **61**, 621 (2003).
5. F. Mecuso, T. Czerwiec, T. Belmonte, L. Dujardin, A. Viola and G. Henrion, *Surf. Coat. Tech.*, **200**, 804 (2005).
6. M.T. Kelly and A. Blaide, *J. Chromatogr. A*, **1134**, 74 (2006).
7. S. Karthikeyan and R. Balasubramanian, *Anal. Chim. Acta*, **576**, 9 (2006).
8. P. Smrkolj and V. Stibilj, *Anal. Chim. Acta*, **512**, 11 (2004).
9. M. Sato, H. Yoshimura, T. Shimmura, H. Obi, S. Hatakeyama, E. Kaneko, H. Hoshino and T. Yotsuyanagi, *J. Chromatogr. A*, **789**, 361 (1997).
10. M. Buchler, T. Watari and W.H. Smyrl, *Corros. Sci*., **42**, 1661 (2000).
11. R. Bonetto, J. Trincavelli and M. Vasconcellos, *Spectrochim. Acta*, **60B**, 1468 (2005).
12. F. El-Hadri, A. Morales-Rubio and M. Guardia, *Food Chem.*, **105**, 1195 (2007).
13. X-Ray Critical Absorption and Emission Energies Chart, HNU-Co X-ray MA, USA.

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