BUILDING MATERIALS AND PRODUCTS

UDC 614.1

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X-RAY FLUORESCENT ANALYSIS OF RUBBER CONCRETE PYROLYSATE

The results of X-ray fluorescence analysis of pyrolysate of rubber concretes (kautons) based on liquid butadiene oligomers of types SKDN-N and PBN. The element compositions of initial and burnt rubber binders are determined.

Keywords: oligomers, X-ray analysis, rubber concretes, kautons, rubber binder.

Introduction

Scientific and technical progress is impossible without modern building materials. Development of new building materials, examination of their properties, manufacturing application, generalization of application experience make up the history of development and production activities of society.

The scientists of Voronezh State University of Architecture and Civil Engineering conducted the researches aimed at development of rubber concretes (kautons).

These rubber concretes are new building composites which use liquid oligodienes hardened with the use of low-temperature sulphur vulcanization. The first researches in this direction were conducted by Yu. B. Potapov and were subsequently developed by the author.

Rubber concrete is the combination of mineral filler and organic binder, namely, with the liquid rubber. Inasmuch as rubber concrete insoluble in standard chemical solvents, the analysis of rubber concretes (kautons) should be conducted after the prior destruction (oxidative, thermal, etc.), by analogy with the rubber [1].

The modern trend in polymer analysis is the analysis of destruction products (mainly of the pyrolysis products). This analysis makes it possible to determine the obtained substances selectively. In this connection it is advantageous to conduct the analysis of rubber concrete elements and the results of its thermal destruction with the use of modern method of analysis, namely, with the use of X-ray fluorescent analysis [2, 3].

On account of structure of rubber concrete and used activators, accelerators and catalysts, we start the analysis of pyrolysis products from the analysis of sulfur content. The sulfur is the basic element for rubber vulcanization.

The analysis of sulfuric vulcanizates involves determination of organic and element, free sulfur, as well as sulfur-containing accelerators.

The analysis of metals entering into the composition of the filler and the aggregate in the rubber concrete [3] is of interest, too. Many metals form compounds of different mechanism of action which retard the polymer combustion. The study of their presence and tentative assessment of their amount in pyrolysis products makes it possible to develop the methods of rubber concrete fire resistance increase.

The basic physical effect X-ray fluorescent analysis based upon is the occurrence of fluorescence in the sample during X-ray irradiation [2, 3].

The spectrum of this secondary irradiation depends on content of elements in the sample. This physical effect is the basis for determination of element composition of the sample from the spectrum of its X-ray fluorescent irradiation, and content of the elements is proportionate to the value of corresponding spectrum lines.

The generation of quanta with energies equal to the differences between the energies of the finite shell from which the electron was removed as the result of ionization, and the shell from which the vacancy was filled.

When the vacancies are formed on the given shell the transfer needed for the filling of the vacancy may proceed from more than one shell, therefore X-ray spectra consist of the whole series of the lines. In accordance with the name of the shell with the vacancy the series is called *K*, *L*, *M*, *N* or *O*.

Each series consists of several lines which are designated in ascending order of irradiation frequency α, β, γ, etc., which in their turn have numeric notations *Kαl*, *Kα2*, *Kβ1*, *Kβ2*, *Kβ3*, *Lα1*, *Lα2*, *Lβ2*, etc.

Sometimes total line which is measured by the spectrometer as one line is designated without numeric notation as $K\alpha$ (or KA).

The linkage between the length of the wave of X-ray spectrum line and atomic number of the exciting element (Moseley law) [2, 3]:

$$I = const \,/\, (Z - \sigma)^2, \quad (1)$$

where I is the length of the wave of exciting line, Z is the atomic number of the element, σ is the shielding constant.

Relative intensity of the lines in the series is determined by the probability of corresponding transfers of electrons between energy levels.

The measurements were conducted with spectrometer "SPECROSKAN MAX-GV".

The qualitative analysis is based on the processing of the measured spectrum of fluorescence from the sample. The purpose of the processing is the total identification of the spectrum peaks, that is, it is necessary to determine which series and element lines spectrum peaks correspond to. This procedure allows the qualitative composition of the sample to be determined. Furthermore, the peak values help to roughly estimate relative content of the elements in the sample.

Spectrograms and conditions of their record are shown in Fig. 1-4.

a)

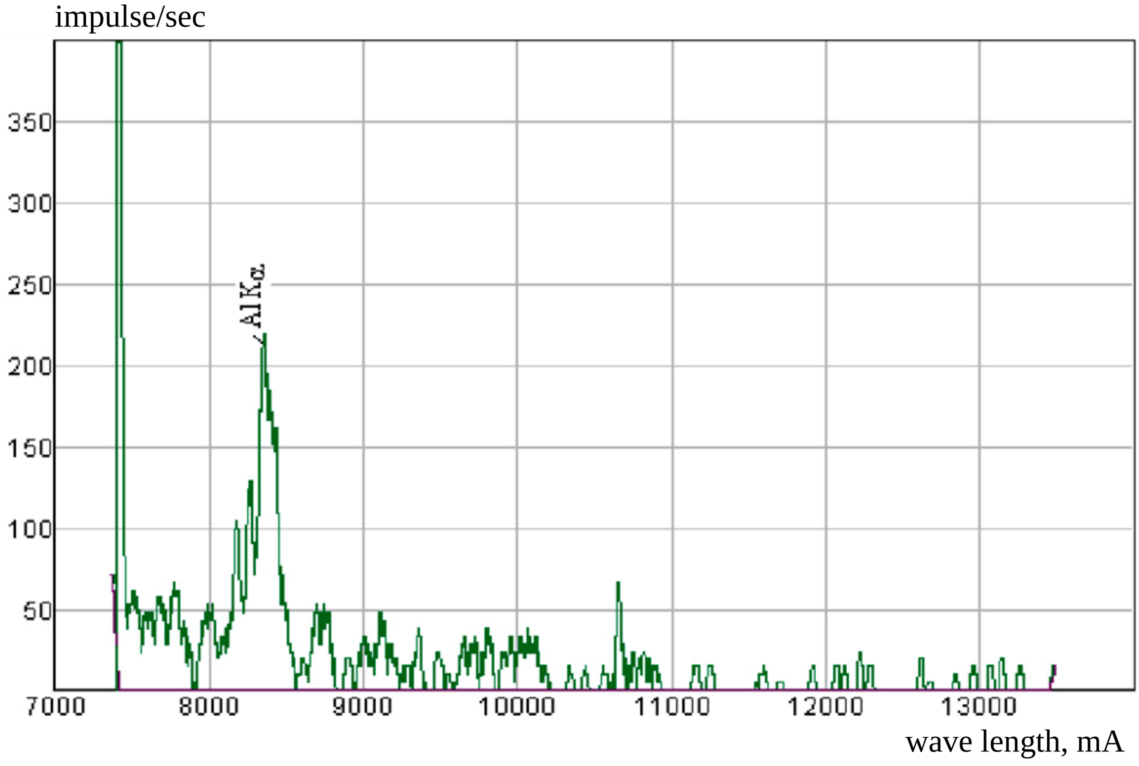
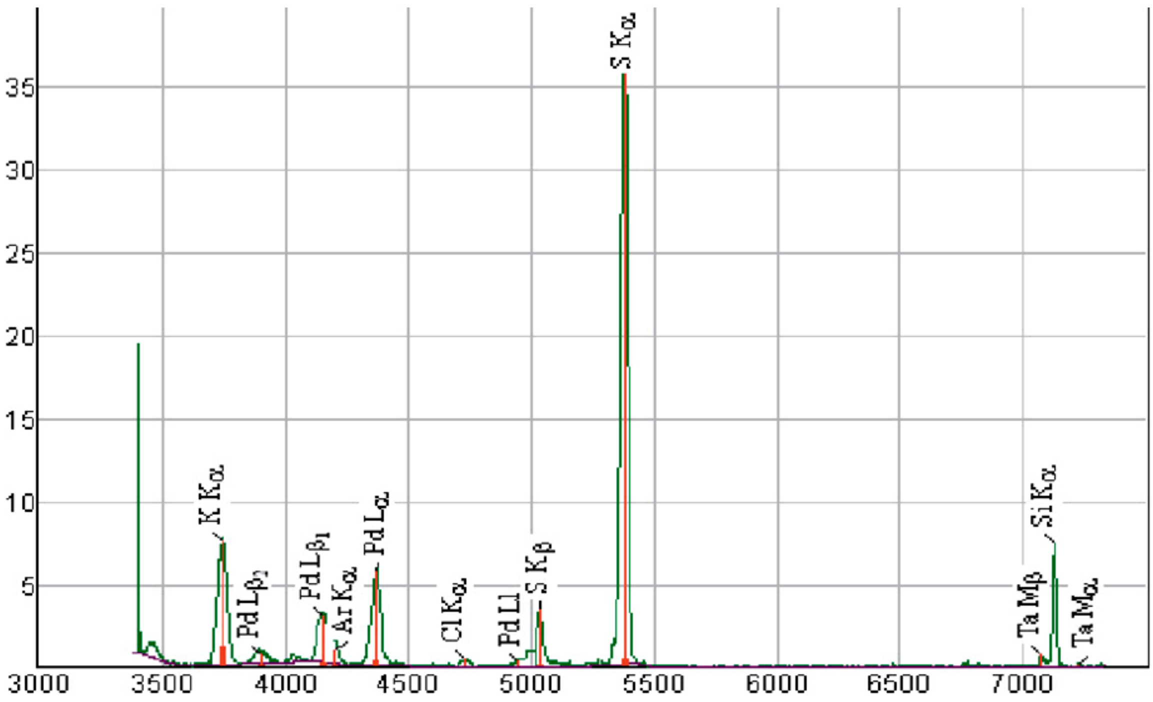


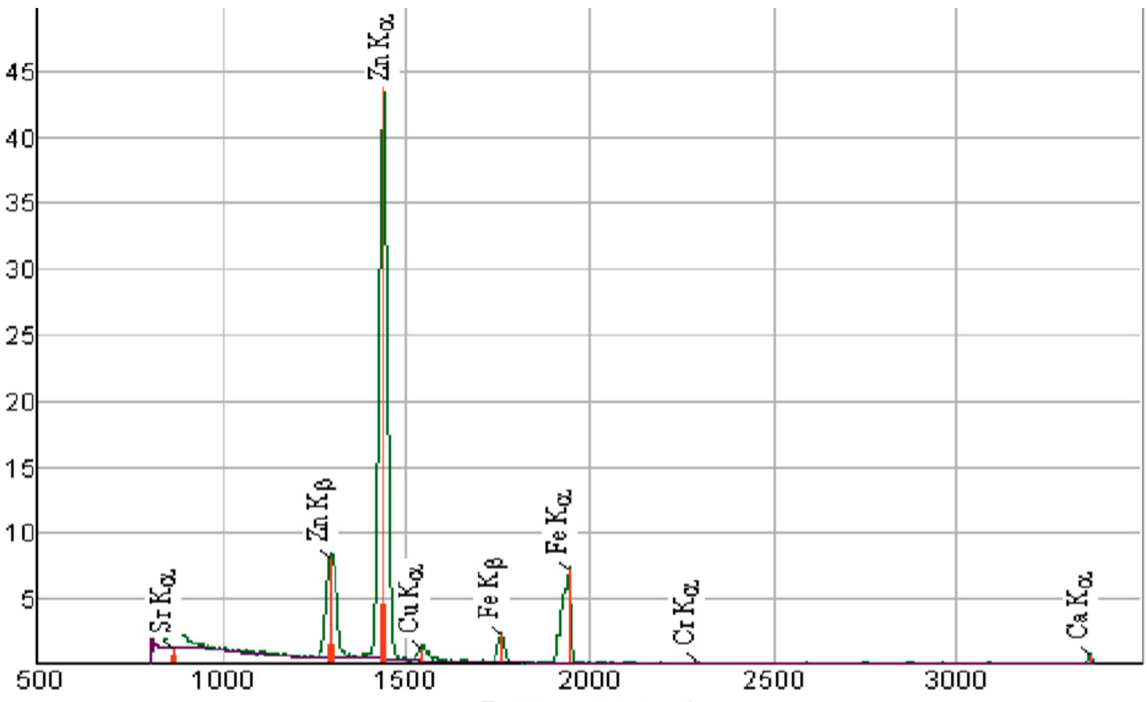
Fig. 1. X-ray fluorescent spectrum of initial sample of rubber concrete (kauton) based on liquid rubber SKDN-N: a) Voltage of X-ray tube 40 kV, current 3.99 mA, exposure 0.212 sec, step 2 mA

b) impulse/sec



wave length, mA

c) impulse/sec



wave length, mA

Fig. 1 (end). X-ray fluorescent spectrum of initial sample of rubber concrete (kauton) based on liquid rubber SKDN-N:
b) Voltage of X-ray tube 40 kV, current 3.99 mA, exposure 0.118 sec, step 2 mA;
c) Voltage of X-ray tube 40 kV, current 0.49 mA, exposure 0.156 sec, step 2 mA

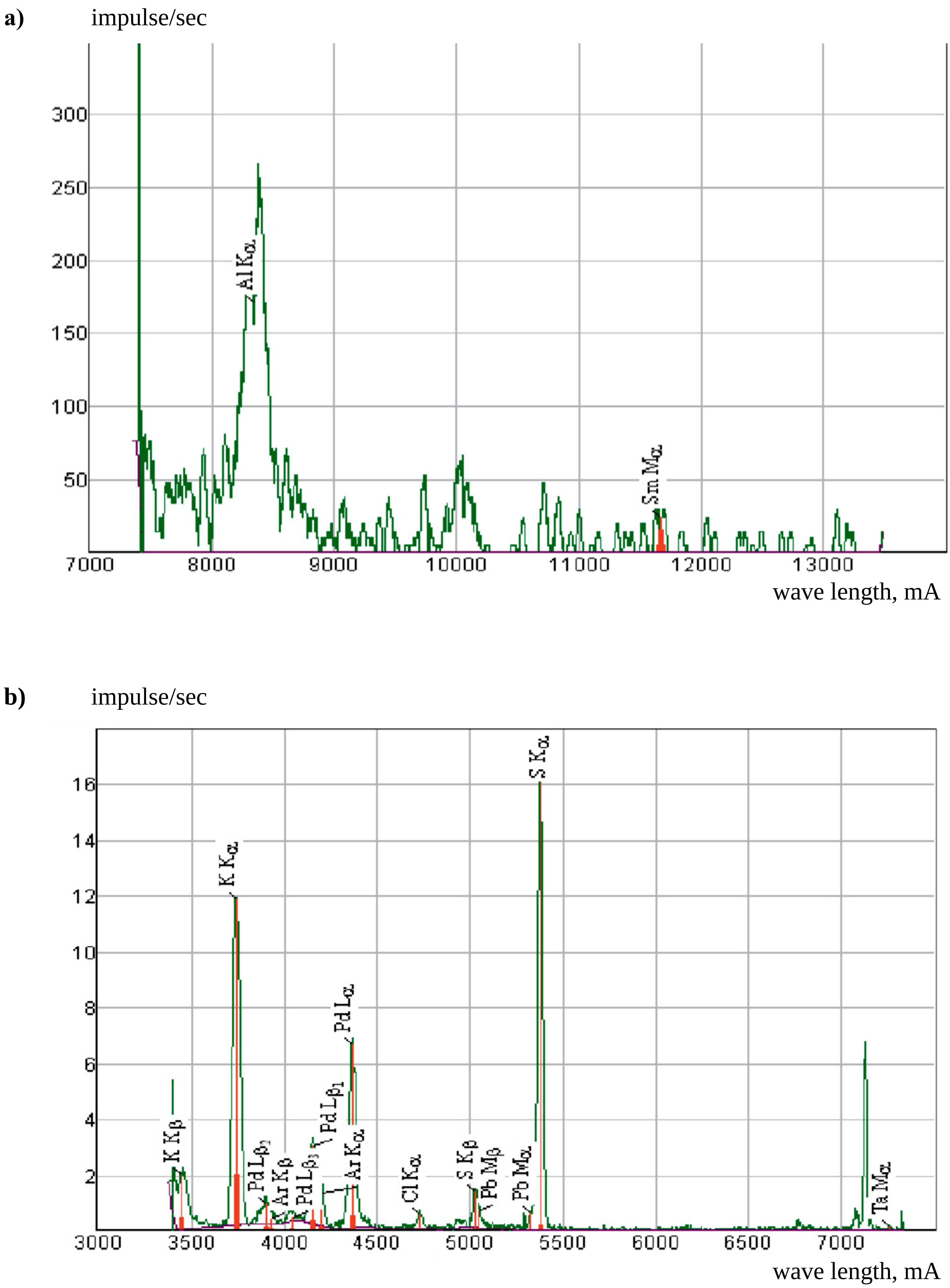
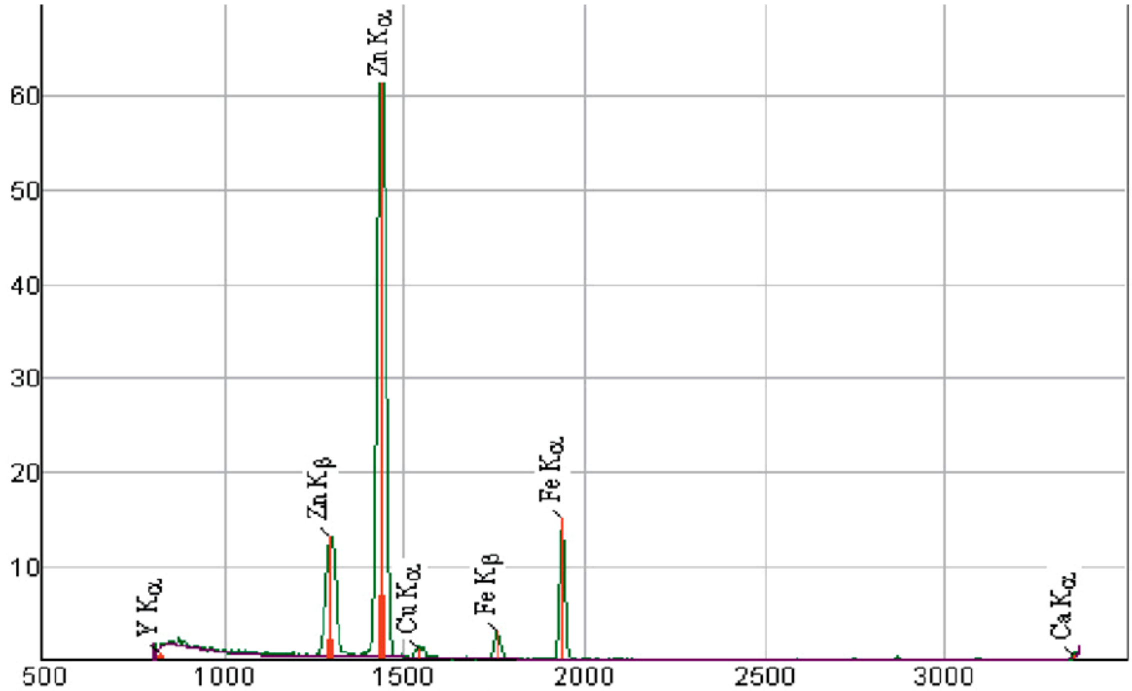


Fig. 2. X-ray fluorescent spectrum of the sample
of burnt rubber concrete (kauton) based on liquid rubber SKDN-N:
a) Voltage of X-ray tube 40 kV, current 3.99 mA, exposure 0.212 sec, step 2 mA;
b) Voltage of X-ray tube 40 kV, current 3.99 mA, exposure 0.1 1 8 sec, step 2 mA

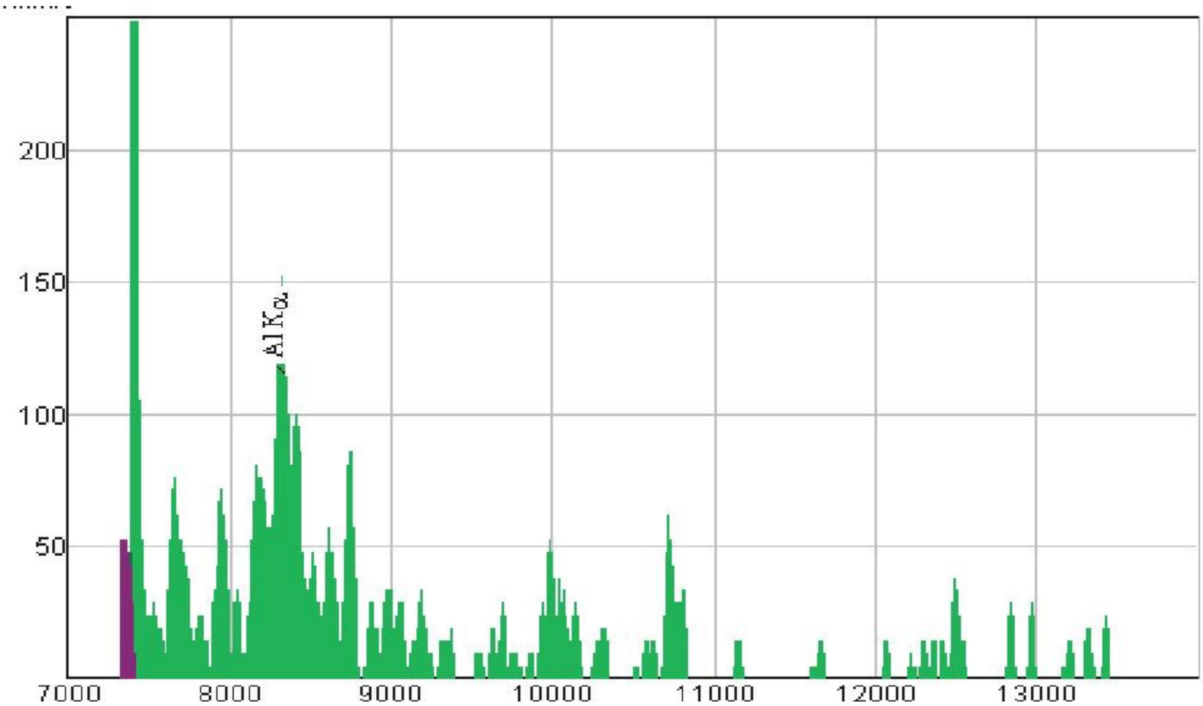
c) impulse/sec



wave length, mA

Fig. 2 (end). X-ray fluorescent spectrum of the sample of burnt rubber concrete (kauton) based on liquid rubber SKDN-N: c) Voltage of X-ray tube 40 kV, current 0.49 mA, exposure 0.156 sec, step 2 mA

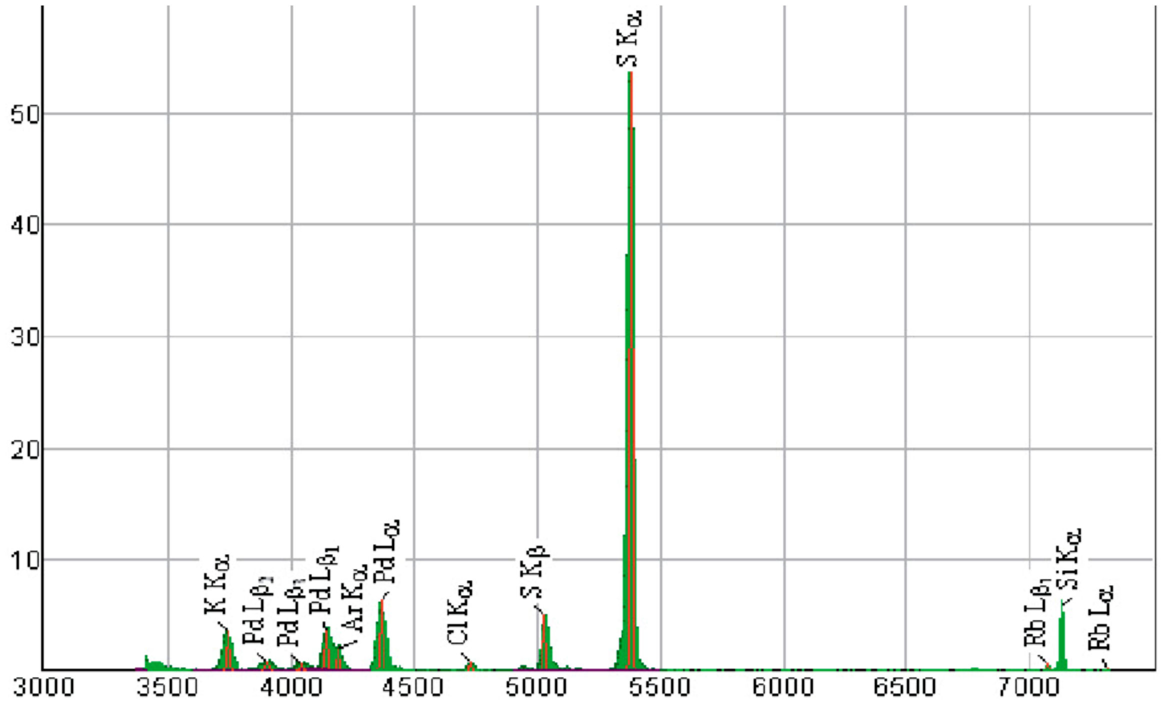
a) impulse/sec



wave length, mA

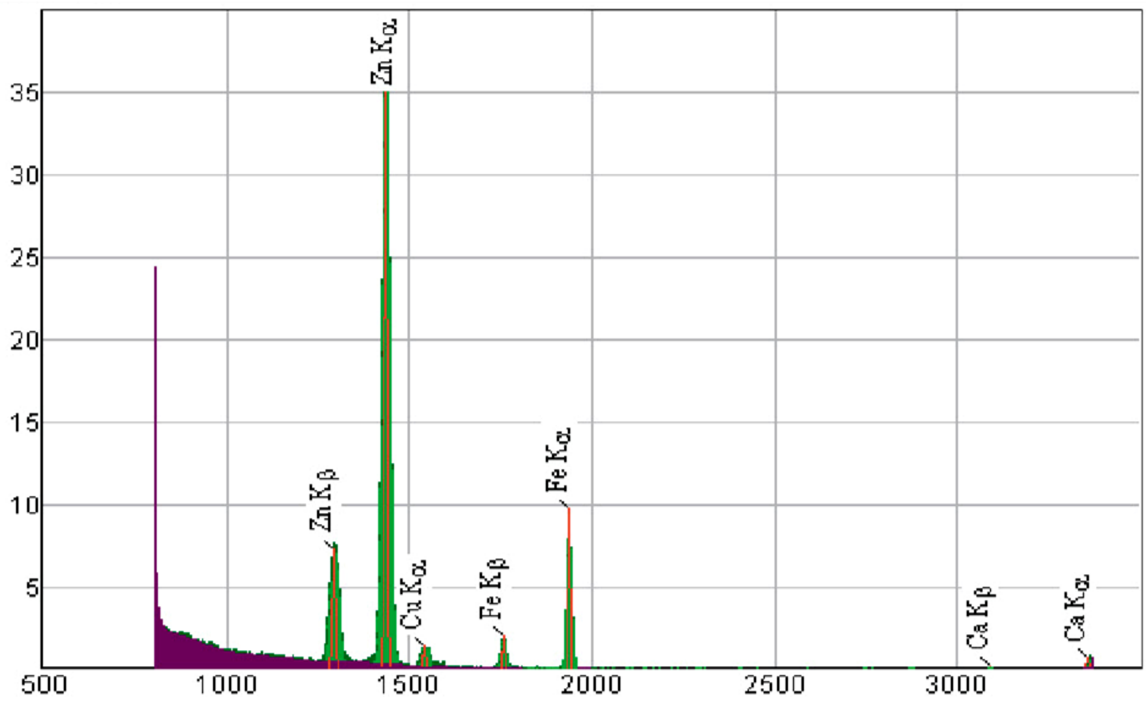
Fig. 3. X-ray fluorescent spectrum of initial sample of rubber concrete (kauton) based on liquid rubber PBN: a) Voltage of X-ray tube 40 kV, current 3.99 mA, exposure 0.210 sec, step 2 mA

b) impulse/sec



wave length, mA

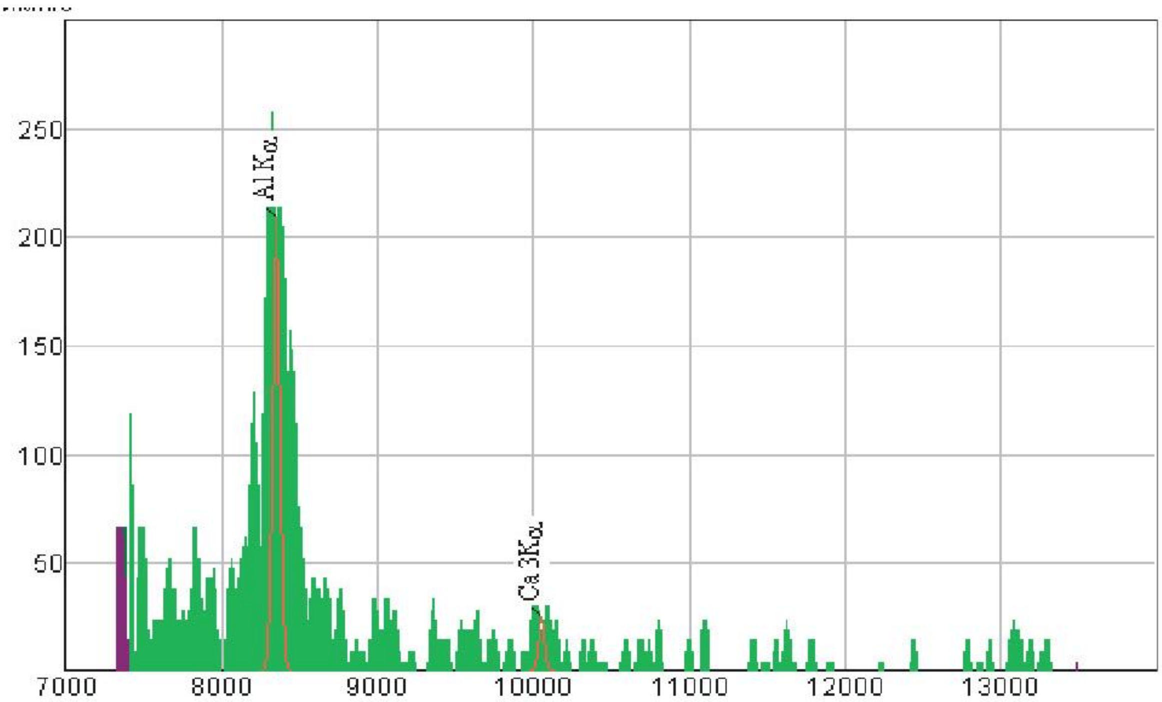
c) impulse/sec



wave length, mA

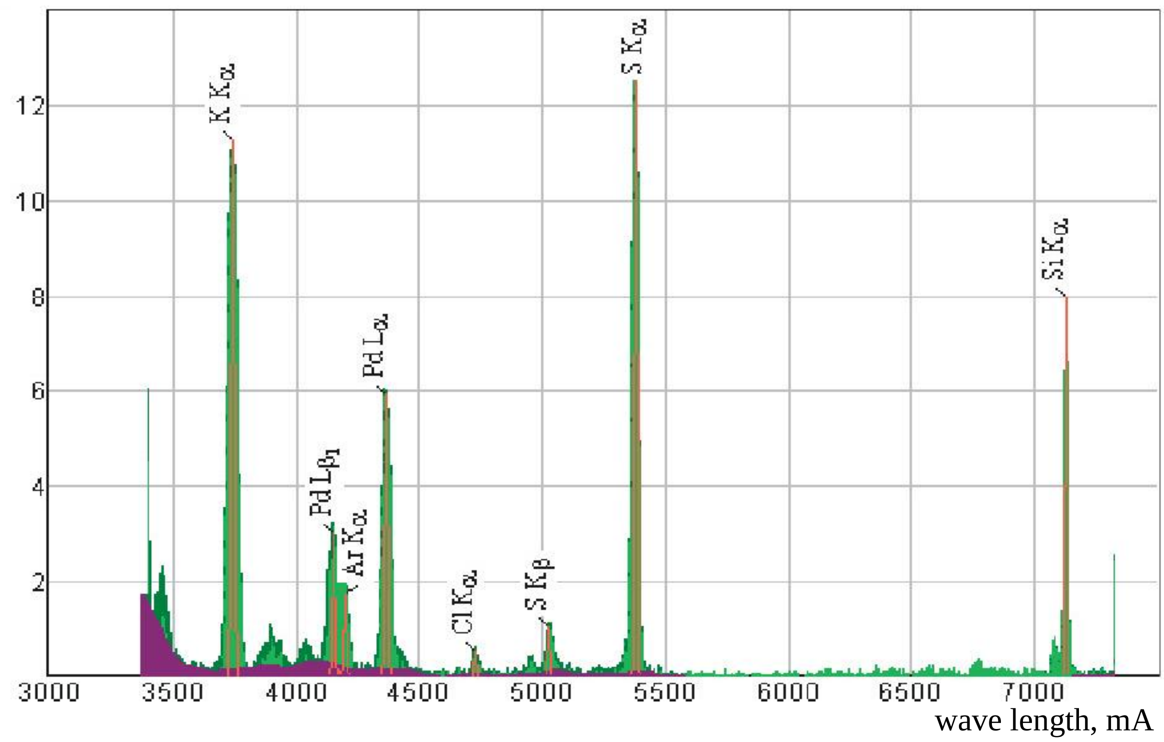
Fig. 3 (continue). X-ray fluorescent spectrum of initial sample of rubber concrete (kauton) based on liquid rubber PBN:
b) Voltage of X-ray tube 40 kV, current 3.99 mA, exposure 0.118 sec, step 2 mA;
c) Voltage of X-ray tube 40 kV, current 0.49 mA, exposure 0.156 sec, step 2 mA

a) impulse/sec



wave length, mA

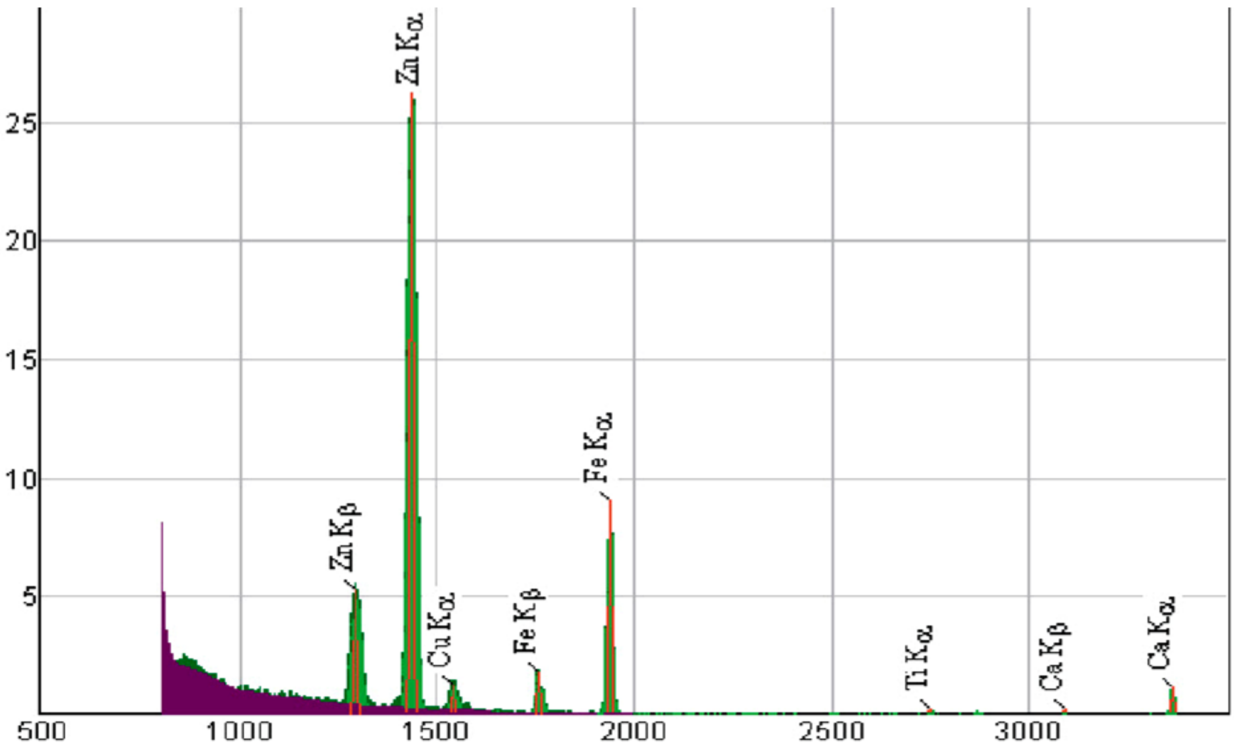
b) impulse/sec



wave length, mA

Fig. 4. X-ray fluorescent spectrum of the sample of burnt rubber concrete (kauton) based on liquid rubber PBN:
a) Voltage of X-ray tube 40 kV, current 3.99 mA, exposure 0.210 sec, step 2 mA;
b) Voltage of X-ray tube 40 kV, current 3.99 mA, exposure 0.1 1 8 sec, step 2 mA

c) impulse/sec



wave length, mA

Fig. 4 (end). X-ray fluorescent spectrum of the sample of burnt rubber concrete (kauton) based on liquid rubber PBN: c) Voltage of X-ray tube 40 kV, current 0.49 mA, exposure 0.156 sec, step 2 mA

Summary

It was established that lines corresponding to the metals don't change for initial and burnt rubber concrete (kautons), which point to the qualitatively constant composition.

The lines of Zn and AL increase their value for burnt rubber concretes. Such behavior can be attributed to the fact that initial amount of metals is constant at pyrolysis. In so doing they may form compounds with warming-resistant pyrolysis products. Organic polymer binder is burning out during pyrolysis, which increases metal content in the formed ash.

Change in metal content in rubber concrete which did not undergo pyrolysis is characterized by twofold increase [4, 5, 6].

The spectrum line describing sulfur in the burnt rubber concrete is three times as weak as the line in initial rubber concrete. Based on relative technique of qualitative analysis of composition of the samples under investigation and taken the amount of

Zn and AL as reference value, we concluded that in burnt rubber concrete total amount of sulfur decreased more than six times. Such correlation is due to the fact that not all sulfur burns at high temperature.

When heated, it forms hard-meltable sulphides which in their maintain loose structure of the external layers of rubber concrete at high temperature, which retards their destruction and slows down internal layer heating [4, 5, 6].

X-ray fluorescent analysis of rubber concrete (kauton) samples and burnt rubber concrete (kauton) samples made it possible to determine qualitative changes in the samples.

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