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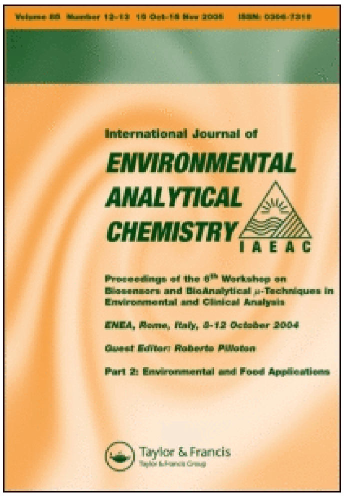

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H. Daiev[a]; ST. Doichinov[a]
[a] Chemical Department, Sofia University "Kliment Ohridski" National Institute of Cultural Monuments,

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Simultaneous Neutron-Activation Determination of Microquantities of 12 Metals in Air from the Surrounding Area of Some Art Monument†

H. DAIEV and ST. DOICHINOV

Chemical Department, Sofia University "Kliment Ohridski" National Institute of Cultural Monuments

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A simultaneous neutron-activation determination of microquantities of iron, cobalt, manganese, zinc, copper, chrome, lanthanum, scandium, gold, platinum, cesium, selenium was carried out in aerosoles of the surrounding area of some art monuments.

The 125 samples analysed that were taken monthly throughout a year gave the possibility to ascertain a great changeability in the concentrations of microcomponents during the different seasons of the year. The content of Fe for instance in the air of the surrounding area of the church Sveta Petka Samardjiiska fluctuates from $1{,}2.10^3$ upto 6.10^3ng/m^3, of Co from 2 upto 41 ng/m^3, of Zn—from 90 upto 2.10^3ng/m^3, of Cu—from 55 upto $1{,}5.10^3$ng/m^3.

The comparison of the results obtained, with the data from different objects abroad confirms the conclusion about changeability in the microcomponents of air samples.

KEY WORDS: Neutron activation analysis, isotopes—^{59}Fe, ^{64}Cu, ^{46}Sc, ^{139}Cs, ^{140}La, ^{56}Mn, ^{191}Pt, ^{198}Au, ^{65}Zn, ^{51}Cr, ^{60}Co, ^{75}Se, simultaneous gamma spectrometric determination, art monuments.

The intensive development of industry, transport and the continuous increase of the population density in cities has led to an increase in the quantity of corrosive vapors in the air. The existence of high concentrations of different gases in the atmosphere (sulphur dioxide, carbon dioxide, carbon monoxide, nitrogen, oxides, etc.,) together with metal catalysts with different activities and being in the vapour state (Fe, Cu, Zn,

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Mn, etc.,) has led to destructive processes in the pigment layer of mural paintings[1,30]. Because of that, determination of metals in air is by all means of great interest. There have been different methods used for the qualitative determination of metal aerosols in air: photometric[3,13], polarographic[2,14], emission spectral[5,7], atomic adsorption[2,5,6,13], X-ray-spectral[2,4,7], X-ray-fluorescent[5,7], mass-spectrographic[2], photoactivation[6], and neutron activation[5–12,15–17,21,25,26,31]. The comparative studies of Coleman[2] show the advantages of the method last mentioned because it has potential for the qualitative determination of more elements, and an exclusive purity of the reagents used after irradiation of samples is not necessary. Some shortcomings of the method are its difficult accessibility, necessity of nuclear reactor, expensive gamma spectrometric apparatus, radio chemical laboratory and all the safety measures necessary for radioactive rays.

The aim of the present project is to test neutron activation for the simultaneous detection of twelve metal components that are in micro and ultramicro concentration in vapours polluting the atmosphere in the vicinity of monuments of art. The solving of that problem is obviously connected with the concentration of these metal components, the nuclear characteristics of the radio-active isotopes resulting from (n, γ) reactions and the resolution of the gamma spectrometric detector apparatus. As a suitable model, objects have been chosen from the Boyana Church and the Church "Sveta Petka Samardjiiska" in the centre of Sofia. This has been done in view of the exclusive value of both objects and the different locations from intensive emitters of air pollution. Certain tests from the Kremikovtzi Monastery have been investigated for comparison. At present we have data for the total dust covering and for some places (Sofia, Pirdop, Varna, Kardjaly) we have data as well for the pollution of air with Pb, Cu, As, SO_2[14,28]. No neutron activation tests on the contents of metals in air samples from the surrounding have been made.

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EXPERIMENTAL PART

1. Taking initial samples and determination of the concentration of dust in them.

The initial samples for dust were taken by means of high debit electro-aspirator A-200. The air was sampled at a speed of $100\,dm^3/min$ and $6000\,dm^3$ were used for each test.

Filter FPP-15 (Soviet production) was used. It was a highly effective filter mass of polyvinylchloride. This filter is characterised with a high collecting capacity of submicroscopic particles with dimensions larger than $1\,\mu m$[4,7,8,13,18,22–24,26].

Simultaneously with sample taking, the temperature in °C and the atmospheric pressure in mm Hg were measured.

The air volume was calculated from the following formula:

1) $V_o = KV_t$

V_t—volume of the air passed through the filter

V_o—recalculated volume of air

K—recalculating factor

2) $K = 273{,}2.P/(273{,}2 + t)760$

P—barometric pressure at the test taking moment

t—temperature at the test taking moment

The concentration of dust (C_d) was calculated in mg/m^3 from the following formula:

3) $C_d = Q.1000/V_o$

Q—the weight of dust on the filter

C_d for the day was calculated as an average of five samples. Throughout 13 months 60 samples were taken from each of the two objects and five samples from the Kremikovtzi Monastery for a total of 125 samples.

Figure 1 shows a used and an unused filter.

Figure 2 gives the calculated dust concentrations in the air samples taken from the Boyana Church, the church "Sveta Petka Samardjiiska" and the Kremikovtzi Monastery. Their comparison with the highest permissible concentrations as per the regulations of our country (0,5 mg/m^3) shows that the dust concentration in the church "Sveta Petka Samardjiiska" is highly above that value.

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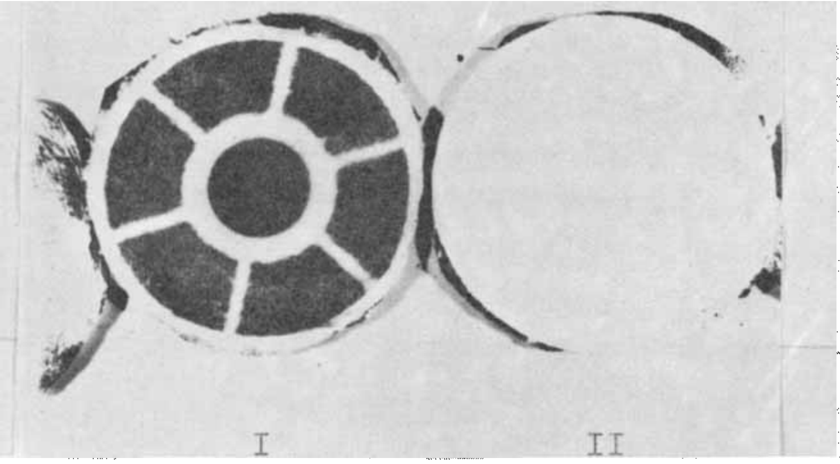

FIGURE 1 Used (I) and unused (II) filter.

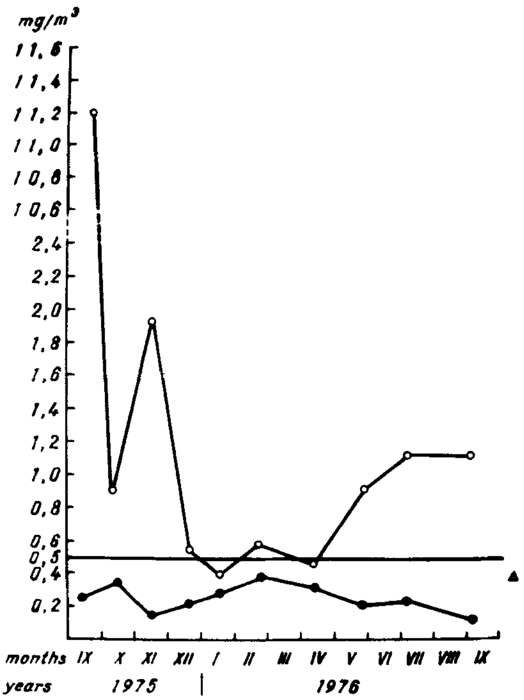

FIGURE 2 Concentration of dust in the air tests taken from the Boyana Church (black dots), the church "Sveta Petka Samardjiiska" (white dots), Kremikovtzi Monastery (triangles) compared PDK (0,5 mg/m^3).

2. Preparation of standard solutions

Twelve elements were selected in the present project: Fe, Mn, Co, Zn, Cu, Cr, La, Sc, Au, Pt, Cs and Se. The initial solutions were made either by diluting of the respective metal (e.g. Zn) or oxide (La_2O_3, CrO_3, MnO_2) in nitric acid (suprapure) or by diluting of the respective chlorides in double-distilled water (CsCl) or in hydrochloric acid (suprapure), ($CuCl_2$, $AuCl_3$, $PtCl_4$). The test solutions were put in polyethylene bags that are well cleaned with nitric acid and distilled water. After that, the solutions were evaporated to dryness by means of an infra red lamp and they were sealed inside the bags.

The samples were prepared by careful burning of the filters in a muffle furnace by slowly increasing the temperature upto 450°C and keeping that temperature for one hour. In this case the organically bound Br in the filter (activating as per the reaction $^{81}Br/n,\gamma/^{82}Br$ and strongly increasing background activity) was removed. The slow increase of temperature led

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at first to gradual clogging of the filter mass and formation of a filter ash where the latter probably played the role of a peculiar matrix which quantitatively held the elements selected by us. The only exception was Se of which 15% was lost—a fact confirmed by the results. After that the burnt sample was stirred in an agate mortar and sealed into a polyethylene bag prepared as in the case with the standards. All bags containing the standards and samples were hermetically closed.

3. Irradiation of samples and gamma spectrometric measurements.

The samples were irradiated in an atom reactor IRI-2000 in a flux of thermal neutrons with a density of $1{,}6.10^{12}$n/cm^2.sec. The nuclear characteristics of the isotopes (the basis for the gamma spectrometric calculations) are given in Table 1).

Preliminary irradiation with standards carried out for different durations (6h, 12h, 18h) at the same level of the neutron flux show that an irradiation with a duration of 12h gives sufficiently high radioactivity of the isotopes.

TABLE I

Nuclear characteristics of isotopes on basis of which have been carried out gamma spectrometric determinations

Element	Isotope	$\tau_{1/2}$	Energy of photopeaks, kev
Fe	^{59}Fe	45d.	1099 1292
Cu	^{64}Cu	12,8h.	1340
Sc	^{46}Sc	85d.	889 1120
Cs	^{134}Cs	2,05y.	605 795,8
La	^{140}La	1,67d.	1596
Mn	^{56}Mn	2,6h.	820
Pt	^{191}Pt	3,0d.	69
Au	^{198}Au	3,15d.	412
Zn	^{65}Zn	243,8d.	1116
Cr	^{51}Cr	2,7d.	320
Co	^{60}Co	5,26y.	1332
Se	^{75}Se	120d.	121 136 264,5

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The gamma spectra of the samples and the standards were made by means of a 4090 channel analyser 8180 Canberr—USA with a Ge(Li) detector. Some determinations of shortlived isotopes (^{56}Mn with $\tau_{1/2}$ $-2{,}6$h) were carried out in the nuclear reactor immediately after irradiation by a 4090 channel apparatus (Histomat, Intertechnique, France).

From the spectra obtained the areas of the photopeaks were calculated by total area:

(4) $A = \sum_{i=1}^{i=r} a_i - (r - 1 + 1)/2(a_r + a_1)$

A—area of the photopeak
a_r—number of pulses in the last right channel
a_1—number of pulses in the last left channel
r—number of the last right channel
l—number of the last left channel

RESULTS AND DISCUSSION

The determination of micro and ultramicro concentrations of different elements in the air obviously requires carrying out of preliminary analysis on the purity of the filter used. Our neutron activation data show that Fe, Cu and Zn were the most essential components of the filter. The concentrations of the metals in the FPP-15 filter are given in Table 2.

TABLE II

Contents in % of the metals investigated in FPP-15 filter

Metal	Contents in %	Metal	Contents in %
Fe	3.14^{-4}	La	less than 10^{-6}
Cu	5.10^{-5}	Au	less than 10^{-6}
Zn	$1{,}5.10^{-4}$	Pt	less than 10^{-6}
Cr	$2{,}2.10^{-6}$	Mn	less than 10^{-6}
Co	$1{,}1.10^{-6}$	Sc	less than 10^{-6}
Se	less than 10^{-6}	Cs	less than 10^{-6}

It is known that fluctuations in the concentration of different metal components in air are considerable[6–8, 14, 24–28]. Our investigations of samples taken immediately one after another (within an interval of 1h) show that these fluctuations rather differ for each element (Table 3). For example Fe fluctuates between 3.10^3 and $5{,}5.10^3$ng/m^3, Zn—between 724 and 114mg/m^3, Cr—between 300 and 735 mg/m^3. The precision of the neutron activation determination was derived from the standards where 19 samples were analysed from each different standard (Cu, Fe, Zn, Co, Cr,

TABLE III

Contents in ng/m^3 of the metals investigated in consecutively taken air samples from the investigated objects

	17.2.1975		23.1.1976		25.12.1975		2.6.1976	
element	f.2	f.3	f.3	f.5	f.1	f.2	f.1	f.2
Fe	4885	5615	3817	4366	3000	5568	5617	5432
Co	37	38	21	25	8	18	40	81
Cu	379	428	300	735	—	331	78	78
Cr	282	30	21	32	57	32	186	303
Pt	13	1	1	7	0,5	1	8	—
Au	5	6	4	2	7	3	5	2
La	35	33	7	14	6	8	5	2
Sc	0,2	0,5	2	2	1	5	4	1
Cs	1	3	7	1	5	2	1	2
Zn	463	1351	1300	310	724	114	657	703
Se	—	—	4	—	5	6	—	—

etc.). The values obtained for the relative standard deviations were from 3,4% to 5,0% which by *t*-factor 2,26 and 95% statistical probability gives us an interval of dispersion from 7,7% to 11,3% respectively and an interval of confidence (for an average value) from 2,4% to 3,6%.

We tried to determine the distribution of the 12 elements on the surface of the filter with view of the simultaneous analysis by different methods of the different elements on different parts of the same filter. For this purpose one filter was cut into 4 equal parts and each of them was analysed under the same conditions. The results are shown in Table 4. It is seen from the

TABLE IV

Contents of the metals investigated in ng in the cut FPP-15 filter

Element	1 part	2 part	3 part	4 part	Total
Fe	1363	1208	2298	1528	6400
Zn	683	940	1100	1246	3894
Cu	92	44	176	19	321
Cr	200	216	330	116	858
Co	32	40	38	—	104
La	3	2,2	2,6	2,6	10,4
Cs	1,2	0,9	1	1,1	4,2
Au	2	7	1	1	11
Pt	2	8	2	6	18
Sc	0,7	0,7	0,9	0,6	2,9

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data that in this case we can not rely on a good precision when analysing the total amount of microcomponents of the different parts of the filter that are equal in area.

The data from the neutron activation analysis concerning the contents of Fe, Mn, Co are shown on Figure 3, Zn, Cu and Cr—on Figure 4, Au and Pt on Figure 5, La and Sc—on Figure 6, Se and Cs—on Figure 7. From this data we can draw the following conclusions.

The metal concentrations in the samples from the church "Sveta Petka Samardjiiska" were considerably higher than those in the Boyana Church (mainly Fe, Mn and Cr). Similar values were observed only in relation to the precious metals and that is probably connected with the fact that the area of the Boyana Church was auriferous.

The change in the concentrations with time was rather great, especially for Fe, Co, Cu, Zn, La and Cs, as seen in Figures 4–8.

The explanation for this wide range of values of microcomponents are probably caused by the changing weather conditions in the area of the Capital. It is quite difficult to draw simple conclusions, though it is

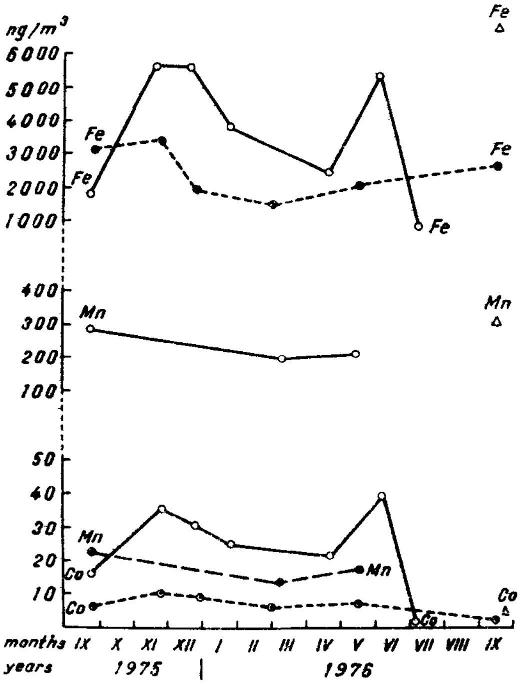

FIGURE 3 Concentration of Fe, Co and Mn in aerosols in air tests from the Boyana Church (black dots), the church "Sveta Petka Samardjiiska (white dots) and the Kremikovtzi Monastery (triangles).

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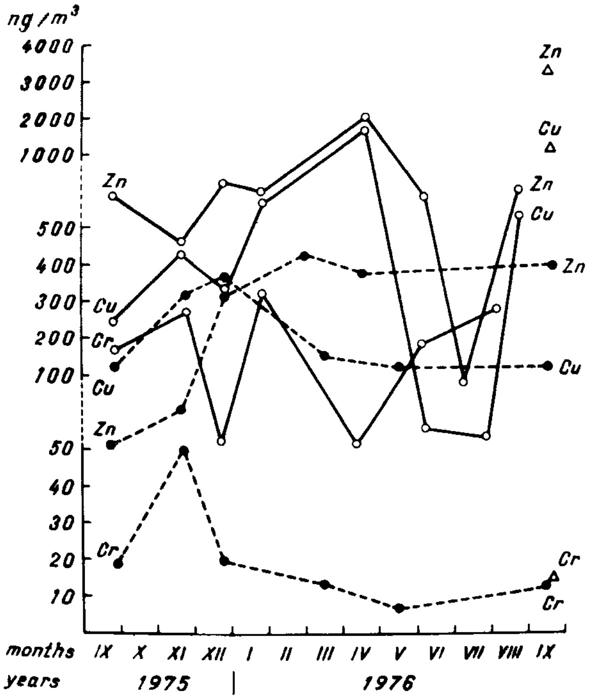

FIGURE 4 Concentration of Zn, Cu, Cr in aerosols in air tests from the Boyana Church (black dots), the church "Sveta Petka Samardjiiska" (white dots) and the Kremikovtzi Monastery (triangles).

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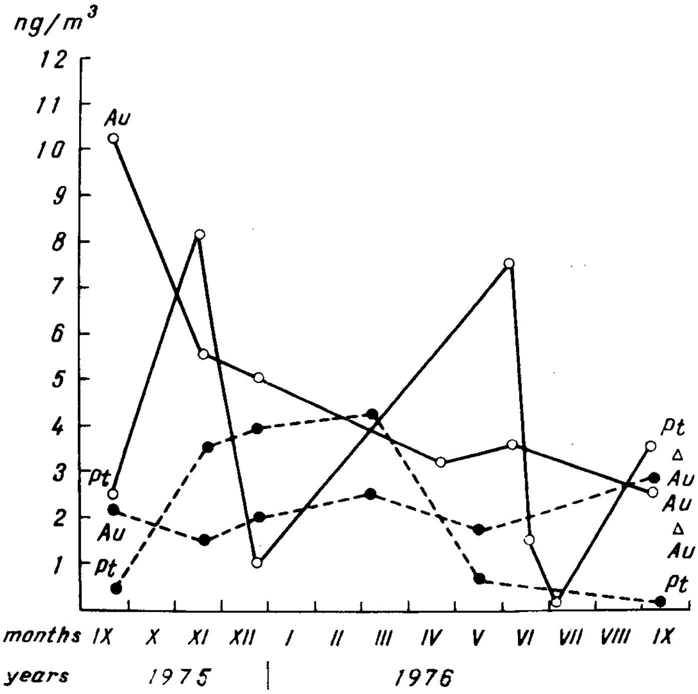

FIGURE 5 Concentrations of La and Sc in aerosols in air tests from the Boyana Church (black dots), the church "Sveta Petka Samardjiiska" (white dots) and the Kremikovtzi Monastery (triangles).

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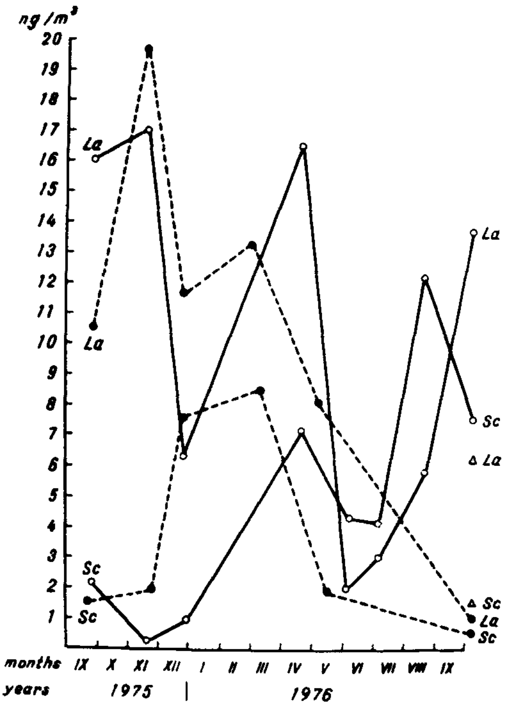

FIGURE 6 Concentrations of Au and Pt in aerosols in air tests from the Boyana Church (black dots), the church "Sveta Petka Samardjiiska (white dots) and the Kremikovtzi Monastery (triangles).

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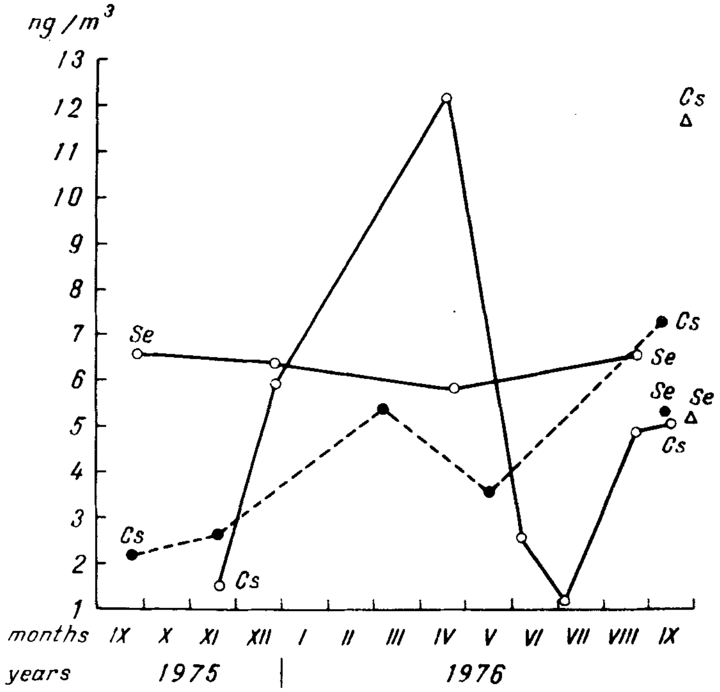

FIGURE 7 Concentration of Cs and Se in aerosols in air tests from the Boyana Church (black dots), the church "Sveta Petka Samardjiiska" (white dots) and the Kremikovtzi Monastery (triangles).

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obvious that in spring and summer the concentration of Fe, Co, Cr and Au decreased and Zn, Cu, La, Pt, Sc, and Cs increased. There are elements like Mn and Se which throughout the whole year do not show great variation in their concentrations.

The comparison of our results with data obtained by other methods and for other objects (air samples) is given in Table 5. This comparison confirms our conclusions about the changeability in the microcomponents of air samples.

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TABLE V

Comparison of our data with the data from literal sources in ng/m^3 literal data

Element	Boyana Church	Church "S.P.S."	Krem. mon.	Bulgaria (14, 28)	USA (27)	Israel (7)
Fe	$1,5.10^3$–$3,5.10^3$	$1,2.10^3$–6.10^3	7.103	–	600–2.10^3	4.10^3–3.10^4
Cu	120–380	55–$1,5.10^3$	$1,3.10^3$	7.10^3–9.10^3	50–9.10^2	–
Zn	50–450	90–2.10^3	3,5–10^3	5.10^3–$9,6.10^3$	100–$1,7.10^3$	17–257
Cr	8–50	52–300	15	–	5–3.10^2	20–130
Co	1–11	2–41	7	–	–	1,6–18,6
Au	1,5–3	2,5–10	3	–	–	–
Pt	0,1–4	0,1–8	3	–	–	–
La	1–20	2,3–17	6,5	–	–	2,1–81,3
Sc	0,5–8,5	0,1–12	2	–	–	1,8–8,9
Cs	2–7,5	0,1–12	11,5	–	–	–
Mn	12–24	200–280	280	500–2.10^3	20–170	53–123
Se	5,5	5,8–6,8	5	–	–	–

Church "S.P.S."—Church "Sveta Petka Samardjiiska"

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TABLE V (cont.)

Comparison of our data with the data from literal sources in ng/m^3 literal data

Element	England (8)	FRG (8)	In the field Chicago	Columbia USA (24)	San Francisco (26)	Canada (6)
Fe	6.10^4–3.10^6	3.104–4.10^6	$1,4.10^4$	$3,9.10^4$	3.10^3	$2,8.10^3$
Cu	8.10^2–6.10^4	–	$1,7.10^3$	–	27–100	7–23
Zn	18.10^3–38.10^4	–	$1,2.10^3$	10^3–2.10^3	27–500	13–450
Cr	640–34.10^3	100–6.10^3	113	41–146	2–44	6–23
Co	800–23.10^3	70–4.10^3	2,6	80–121	0,6–1,7	–
Au	–	–	–	–	0,3–1,3	–
Pt	–	–	–	–	–	–
La	–	–	5,9	29–60	0,8–3,1	0,4–1,4
Sc	11–700	10–850	3,1	4,5–10	0,5–26	0,2
Cs	28–720	–	–	–	–	–
Mn	$1,2.10^3$–77.10^3	5–77.10^3	255	163–$1,5.10^3$	5–34	1,2–5
Se	1,7–3,0	200–1600	–	3,8	9–33	–

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