DETERMINATION OF THE TOXIC TRACE ELEMENT CONTENT OF INDUSTRIAL WASTES BY X-RAY FLUORESCENCE ANALYSIS WITH ISOTOPE EXCITATION. INVESTIGATION OF PAINT WASTES

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Summary

The concentration of the metal components of wastes originating from paints used in various fields was determined, with particular regard to toxic elements.

It was established on the basis of measuring results that wastes generally contain more than one toxic element in different quantities. These elements reveal different mobilities in media of different pH, so that the probability of their getting into the environment considerably varies for the single elements.

The deposition of wastes of this type on the soil can be considered as safe, if the migration of the toxic elements is reduced to a minimum.

Introduction

Several authors were engaged already earlier in the XRF determination of air and water pollution [1–10].

The consequences of making use of the third medium, the soil, the land, sometimes without due circumspection — e.g. indiscriminate deposition of industrial, agricultural and other wastes — were manifested only later. Owing to the increasing protection of air and water, an increasing ratio of wastes was deposited on or in the soil. The deposition of mostly solid and muddy wastes of various origin can result that the inorganic and organic pollutants, e.g. heavy metals, contained in them, get in a longer or shorter time, depending on their mobilizability under the given conditions, into the surface and ground waters. Cause for alarm is also the fact that the migration of the pollutant below the surface is a very slow process, and the long-range sanitary and oecological effects of large quantities of solid wastes are not yet accurately known. Solid environmental samples were analysed by several authors [11–20].

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Dangerous wastes, as e.g. sludges and sludgelike wastes formed mainly in industry prove to be particularly harmful, and their treatment often requires special processes.

Substances of such character are surface coating substances, varnishes, paints used in increasing quantities, which contain both organic and inorganic components. These appear in the waste, and in the case of inadequate waste treatment their polluting effect on the environment must be reckoned with.

Products of the varnish and paint industry, further most of the paint wastes are fire- and sometimes explosion-hazardous, and have at the same time a toxic effect. The harmful effect of the great number of surface coating substances — about two thousand kinds — is of different extent, as the chemical properties of the components and their ratio are also different. Depending on the special field of application, they contain various colouring, filling and binding substances, solvents, plasticizers and auxiliary substances. These comprise many substances of organic or inorganic origin, which, getting into the organism, cause already in small quantities transitory or permanent changes in the metabolic process, or in the colloidal state and physical-chemical structure of the cells and tissues.

Most of the varnishes and paints are colloidal systems, in which the component inducing colour sensation is generally some dye or pigment. Pigments are fine-grained coloured substances, insoluble both in water and solvents, which have adequate physical and chemical properties, and can be used with bonding materials for the preparation of paints, suitable for the coating of surfaces. In the paint industry the value of the pigments depends partly on their chemical structure, and partly on their physical properties. As the use of pigments is multifarious, requirements to be met are also manifold. There is no "universal" pigment, which would simultaneously satisfy all the industrial branches using it. The most suitable one must always be selected according to the requirements of the intended purpose; for example, in thermosetting enamels the pigment is exposed to high temperatures, so that thermal resistance is very important in this case. Distemper paint must satisfy quite different requirements. They are not exposed to thermal action, but the alkaline effect of fresh plaster may decompose the pigment, if it is not resistant to alkalies.

From the point of view of use, inorganic pigments are more important, than organic pigments. The majority of the former is some kind of metal compound, as for example pigments containing barium, zinc, cadmium, lead, iron, copper, titanium, chromium, molybdenum, cobalt and manganese. It can be noted from this enumeration, not aimed at completeness, that a substantial part of the metals contained in inorganic pigments is toxic. In the wastes formed during the application and removal of surface coating substances, generally several components of the coating substances, thus pigments are present. The further fate of these wastes is decisively determined by the qualitative and quantitative distribution of the components, and their chemical and physical-chemical properties.

Samples analysed

Tests were carried out on wastes formed during the use of surface coating substances, suitable for different purposes:

H1 — Sludge formed from primer point used in bus plant.
H2 — Muddy waste of paint used in bus plant.
H3 — Waste of anticorrosive coating.
H4 — Enamel paint waste.
H6 — Motor car enamel waste.
H7 — Paint waste.
H8 — Paint waste.

Samples were taken by the Central Laboratory of the Institute for Environmental Protection, then sent to the Department for analysis.

Preparation of the samples

The available XRF measuring instrument makes possible the qualitative analysis and the quantitative determination of the composition of solid substances, or of grindable, homogenizable substances, which can be brought with relative ease into solid state, without chemical conversion, destructive treatment of the samples. When using other methods of analysis, samples of this character must be generally subjected to dry or wet destruction, digeration, which requires relatively longer and more composite preparatory operations.

Preparation of measuring tablets for X-ray fluorescence analysis

Samples H1–H8 were kept in a drying oven at 105 °C. After homogenization and crushing first in a porcelain then in an agate mortar, measuring tablets of 0.3 g and 10.6 mm diameter were prepared from samples H1 and H2. From samples H3–H8 measuring tablets were prepared after ignition in a similar way, and these were used for qualitative and quantitative analysis. From tablets H3–H6 a layer of ~1.5 mm thickness, dried for 1 week at 105 °C, was also prepared on aluminium foil, and from this discs of 30 mm ∅ were used for qualitative analysis.

Experimental conditions

The XRF method is well known from literature [21–23]. For the excitation of the samples ^{125}I ring source was used from 3.6 keV to 24 keV. In the energy range above 24 keV, ^{241}Am ring source was used. Energies of the K and L lines of the elements investigated are contained in Table 1. The block scheme of our measuring equipment is shown in Fig. 1.

Table 1

Element	Z	Energies of the characteristic X-lines (keV)				
		K_α	K_β	L_α	L_β	L_γ
Calcium	20	3.691	4.012	0.341	0.344	–
Titanium	22	4.510	4.931	0.452	0.458	–
Chromium	24	5.414	5.946	0.571	0.581	–
Iron	26	6.403	7.057	0.704	0.717	–
Zinc	30	8.638	9.571	1.009	1.032	–
Strontium	38	14.164	15.834	1.806	1.872	–
Zirconium	40	15.774	17.666	2.042	2.124	2.302
Cadmium	48	23.172	26.093	3.133	3.316	3.716
Tin	50	25.270	28.483	3.444	3.662	4.131
Barium	56	32.191	36.376	4.467	4.828	5.531
Mercury	80	70.821	80.258	9.987	11.823	13.828
Lead	82	74.957	84.922	10.549	12.611	14.762

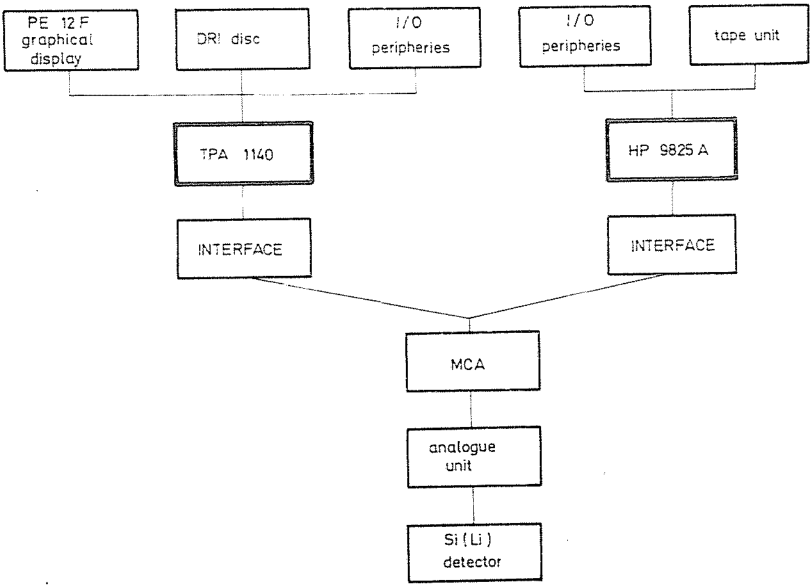

Fig. 1. X-ray fluorescence measuring data-gathering and -processing system

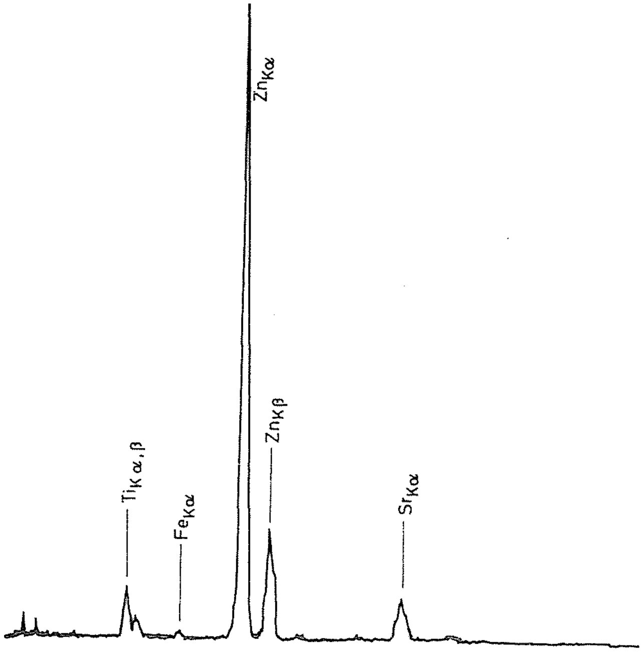

Fig. 2. X-ray spectrum of sample H1, excited with ^{125}I source

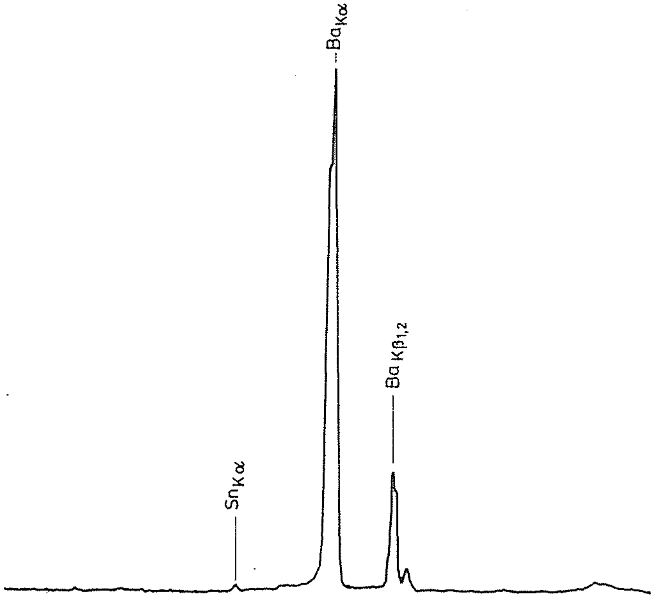

Fig. 3. X-ray spectrum of sample H1, excited with ^{241}Am source

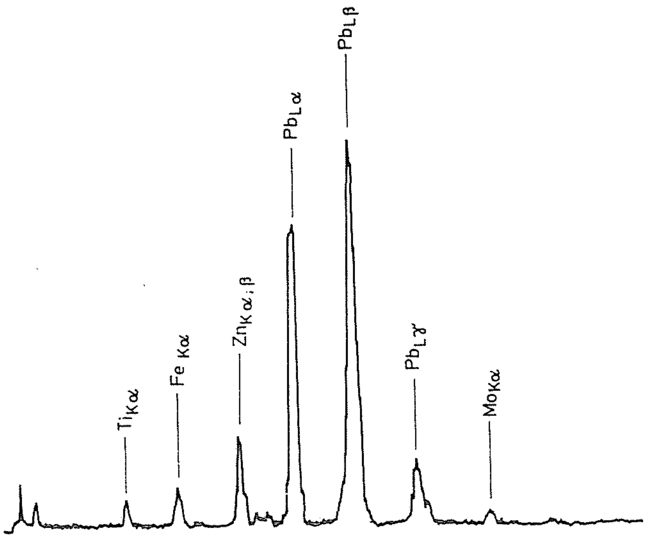

Fig. 4. X-ray spectrum of sample H2, excited with ^{125}I source

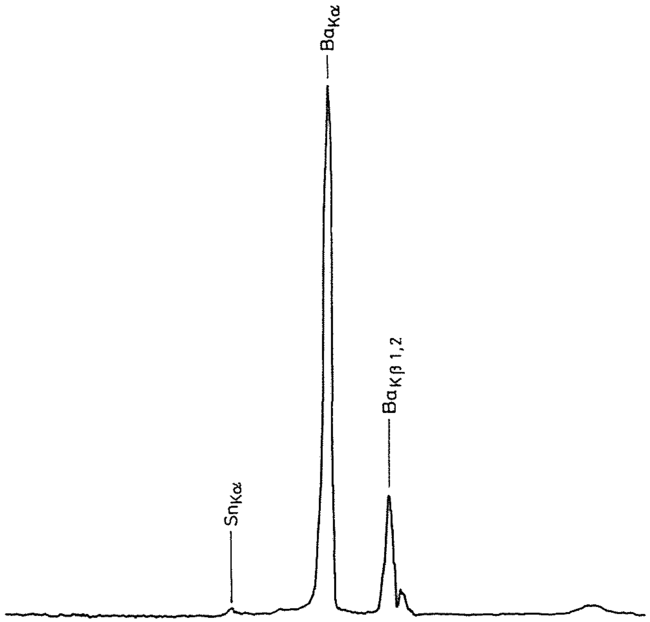

Fig. 5. X-ray spectrum of sample H2, excited with ^{241}Am source

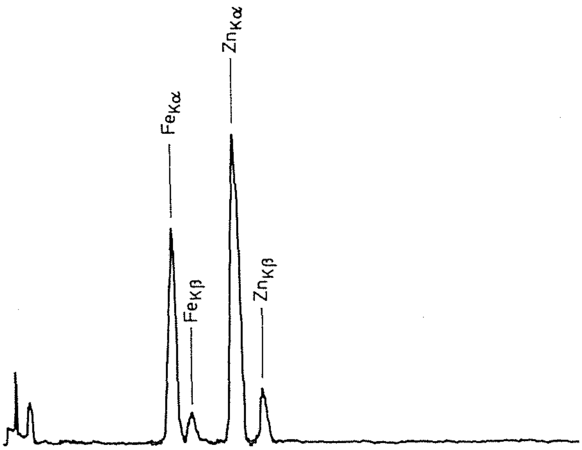

Fig. 6. X-ray spectrum of sample H3, excited with ^{125}I source

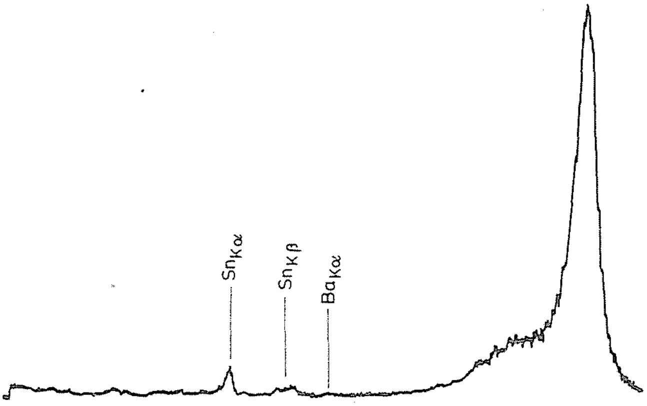

Fig. 7. X-ray spectrum of sample H3, excited with ^{241}Am source

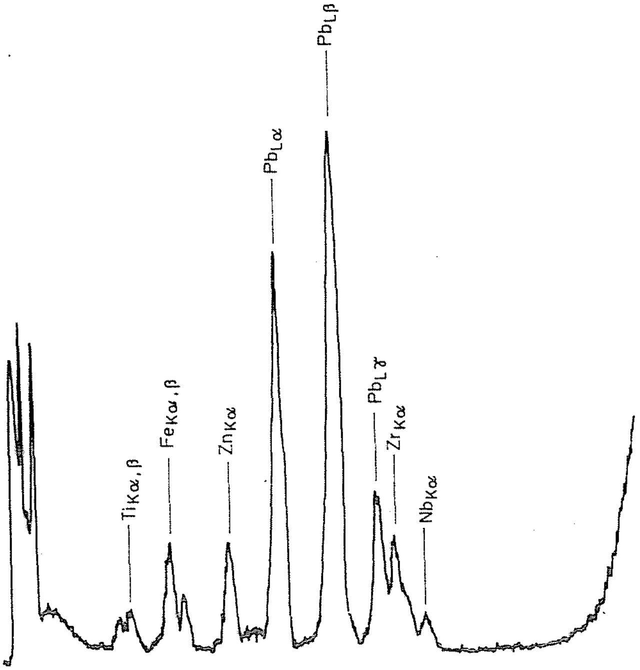

Fig. 8. X-ray spectrum of sample H4, excited with ^{125}I source

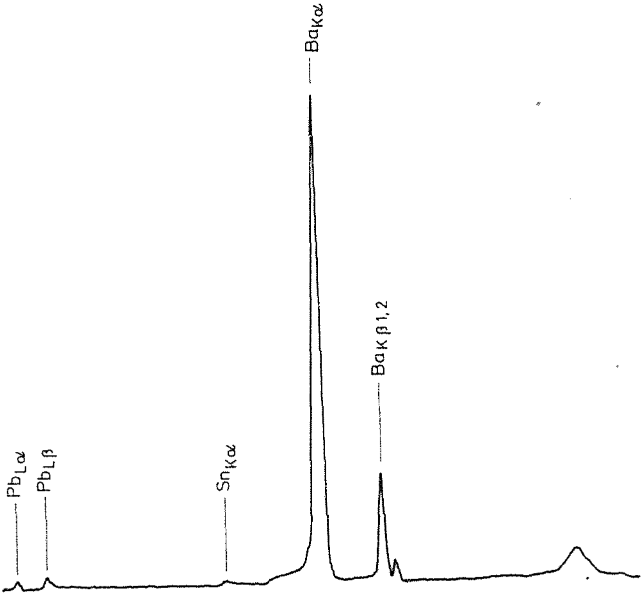

Fig. 9. X-ray spectrum of sample H4, excited with ^{241}Am source

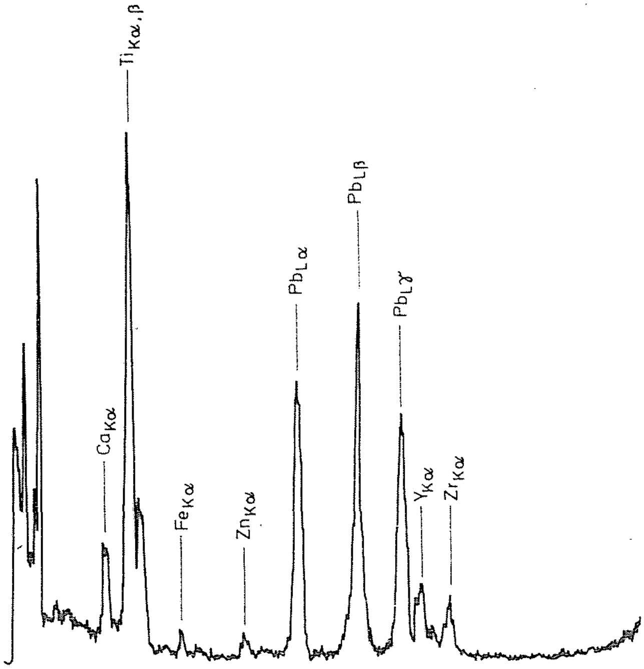

Fig. 10. X-ray spectrum of sample H5, excited with ^{125}I source

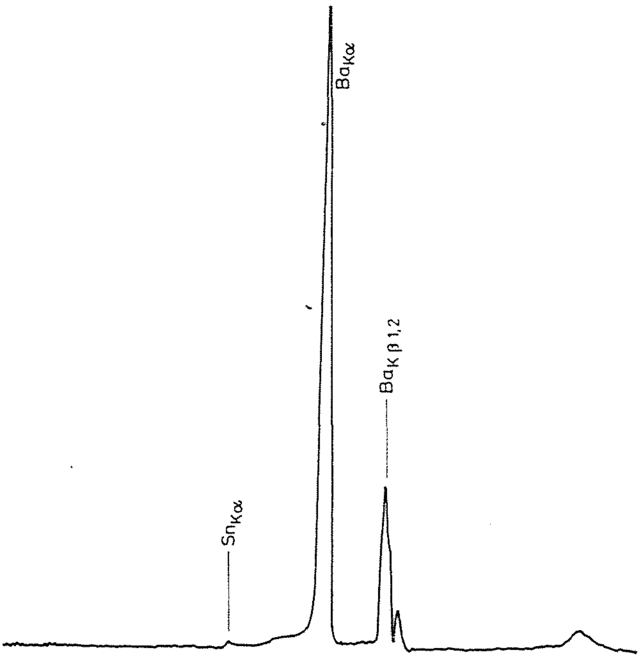

Fig. 11. X-ray spectrum of sample H5, excited with ^{241}Am source

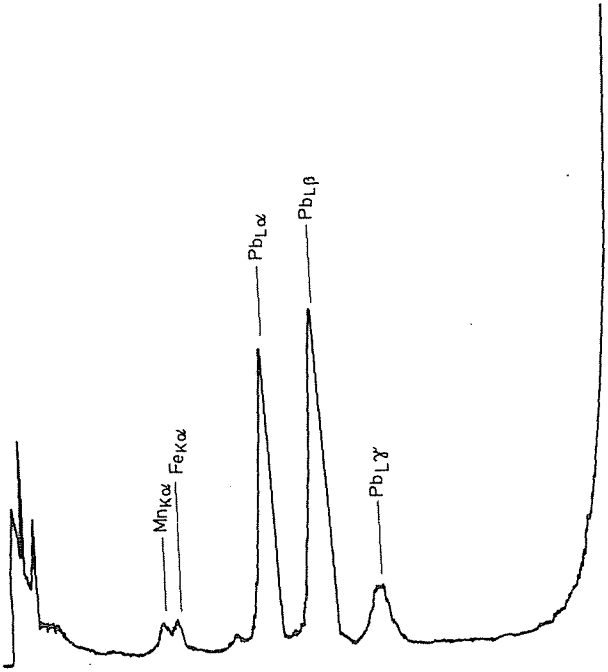

Fig. 12. X-ray spectrum of sample H6, excited with ^{125}I source

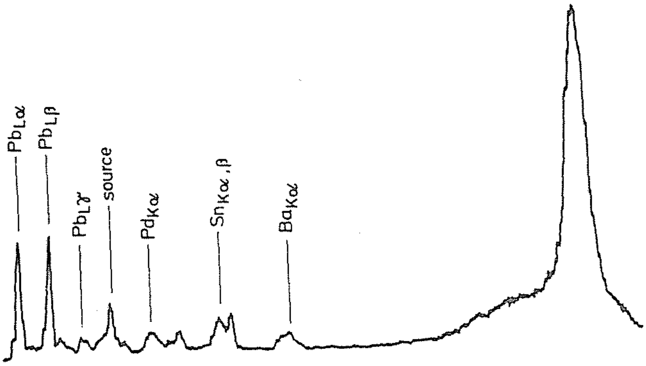

Fig. 13. X-ray spectrum of sample H6, excited with ^{241}Am source

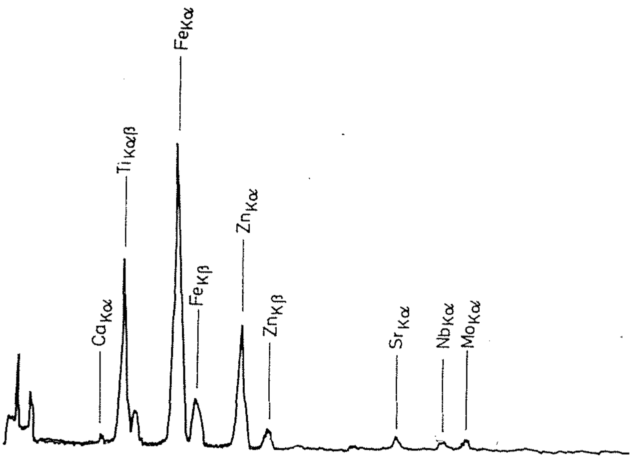

Fig. 14. X-ray spectrum of sample H7, excited with ^{125}I source

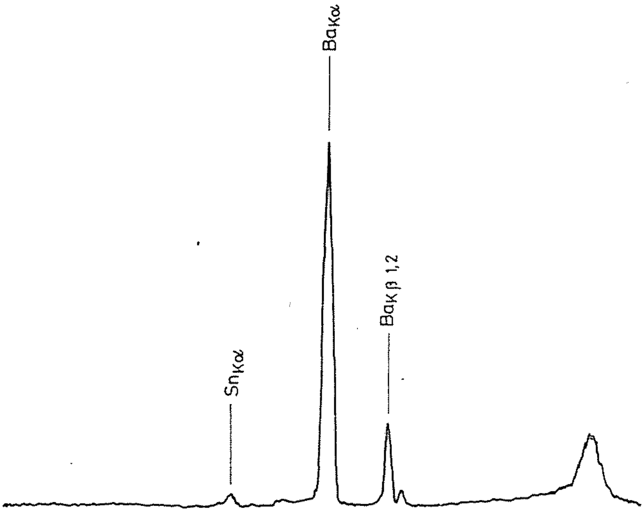

Fig. 15. X-ray spectrum of sample H7, excited with ^{241}Am source

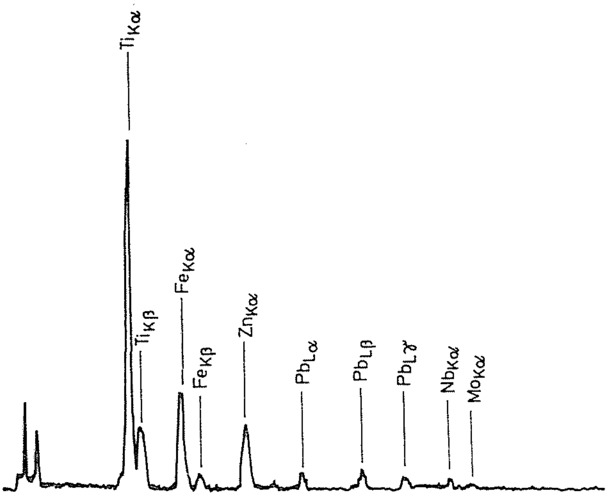

Fig. 16. X-ray spectrum of sample H8, excited with ^{125}I source

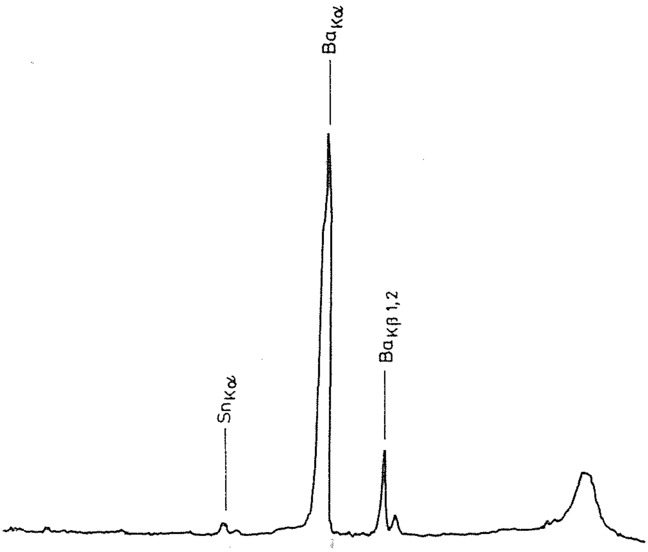

Fig. 17. X-ray spectrum of sample H8, excited with ^{241}Am source

Spectra of the single samples, excited with ^{125}I and ^{241}Am, are shown in Figs 2–17.

The concentration of the single components was determined by element addition. Concentration — intensity data were evaluated by linear regression analysis. Results of the quantitative analysis of the samples are contained in Table 2.

Results were checked with the AAS method, and within experimental error good agreement was found.

Table 2

Quantitative distribution (%) of the components of the samples investigated

Atomic number	20	22	24	26	30	38	40	48	50	56	80	82	Volatile at 105 °C
Sample	Ca	Ti	Cr	Fe	Zn	Sr	Zr	Cd	Sn	Ba	Hg	Pb	
H1	0.91	0.50		0.5	14.4	0.2	0.01	0.01	0.6	25.5	0.02	0.1	18.0
H2		0.3	0.4	1.6	1.2		0.01	0.2	0.1	1.5		11.7	24.0
H3			0.1	3.1	2.0				0.4	0.3			55.8
H4		0.2			0.1				1.7	28.7		0.3	49.9
H5	0.1	0.7		0.2		0.1	0.01		3.0	41.0		0.1	22.2
H6				0.4								2.0	46.9
H7		12.8		4.7	1.0				0.2	2.6		0.1	35.0
H8		22.5		1.4	0.4				0.2	2.4		0.5	52.9

Evaluation of the results

It may be seen from data in Table 2 that the major part (~70%) of the components analysed is toxic element, and each waste sample generally contains more than two of these, in different quantities. Wastes in which toxic elements are present in 5%, 10%, or in some cases even in higher concentration, merit special attention. On the basis of the measuring results the frequency in the samples of the elements investigated, with particular view to toxic elements, can be given.

Fe, Sn, Ba, Pb	88%
Ti, Zn	75%
Zr	38%
Cr, Cd, Sr	25%
Hg	13%

Generally, these elements do not occur singly, but in some combination. Characteristic of their quantitative distribution is that their lowest concentration is 1000 μg/g, or more. The total quantity of components measured by XRF analysis in the wastes was 2.4 to 45.3%.

The single wastes reveal on the basis of the qualitative distribution of the components a certain similarity, but at the same time, the ratio of the components varies within wide limits. This can be attributed on the one part to the use of surface coating substances for a given purpose, depending decisively on chemical composition. On the other part, since the samples analysed, are wastes, they can be "contaminated" by foreign substances of not-paint origin, and depending on their composition and quantity, these may affect the qualitative and quantitative distribution of the components occurring in "pure" paint wastes. This may result in a "dilution" of the toxic elements, but also in an increase of their quantity. Results of our elution investigations will be reported in another paper.

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