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Chemical X-Ray Fluorescence Trace Analysis

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The results of recently published work on the determination of traces of elements by X-ray fluorescence (XRF), combined with chemical methods of separation and concentration, have been reviewed. The application of various combinations of XRF with precipitation, sorption, and extraction has been described. The combined XRF method can be used to determine traces of elements in natural and industrial materials.
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I. INTRODUCTION

In the determination of traces of elements by X-ray fluorescence (XRF), there are several ways of increasing the sensitivity. One is by improving the quality of the apparatus and by using new and more sensitive X-ray spectrometers. This method is not always possible, however, and often does not give the desired results. Thus in a large number of recent studies, the sensitivity of XRF analysis has been increased by preliminary physicochemical and chemical concentration of the elements being determined. Concentration combined with XRF is also convenient in that specimens of uniform composition and form are obtained; this eliminates the complex calculations required to take account of matrix effects.

The following methods are used for concentration in chemical analysis: extraction, sorption, precipitation, evaporation, electrochemical methods, crystallisation processes, zone fusion, and various others[1]. Only those methods of concentration giving specimens convenient for XRF spectrometry are combined with XRF, however.

II. COMBINATION OF X-RAY FLUORESCENCE ANALYSIS WITH PRECIPITATION

The combination of precipitation with XRF determination gives good results, since preliminary separation and selective precipitation make it possible to separate traces of elements from a matrix and also from elements giving interfering spectral lines. On the other hand, the precipitated elements are uniformly distributed in the light matrix of the emitter on a comparatively large surface, increasing the accuracy and sensitivity of the determination.

In an examination of the results of studies based on the combination of precipitation with XRF, mention must first be made of a paper published in 1963 by Luke[21], who showed that this combined method makes it possible to determine traces of 69 elements in organic and inorganic materials, and examined in detail the problems associated with the precipitation, coprecipitation, and filtration of the precipitates, the influence of interfering ions, the use of different precipitants (carbamate, Cupferron, NH_3, H_2S, phenylfluorone); the conditions for the chemical separation of 25 elements and their X-ray analysis were also examined. Luke showed that the method is fairly rapid and sensitive, and makes it possible to determine 2×10^{-8} g Ni, Ti, and Sc; 10^{-7} g Ca, Cu, Fe, Co, and Zn; and 10^{-6} g of a number of other elements.

Another fundamental paper in this field was published by Hirokawa[3], who clearly showed that the combination of XRF with concentration by precipitation is effective and has a high sensitivity. Other studies in this field can be formally divided into two groups, involving the use of inorganic or organic compounds.

1. The Use of Inorganic Precipitants

Traces of elements are usually precipitated as the sulphides, sulphates, or hydroxides. Precipitates of inorganic salts and hydroxides are readily analysed by XRF. It should be borne in mind, however, that possible agglomeration of the precipitate may lead to distortion of the surface of the emitter, with an undesirable effect on the results of the analysis. To prevent this phenomenon, it is recommended that sulphide precipitates be filtered immediately after precipitation. The precipitation of inorganic compounds is widely used for the XRF determination of traces of many elements.

Thus, in the analysis of metallic aluminium for traces of Cu, Fe, Mn, Zn, and Co, the precipitation of these elements as the sulphides made it possible to determine their concentrations at the 10^{-4}% level[4].

An interesting method for determining Hg, Ag, Cu, Bi, Pb, Cd, Se, Te, Zn, Co, and Ni in aqueous solutions is based on the filtration of the solution through a thin layer of zinc and manganese sulphides; the metals listed form less soluble sulphides, and remain in the precipitate, which is then analysed by XRF.[5] In addition to traditional methods of precipitating metals as the sulphides, their determination in precipitates of hydroxides[6-8], oxides[9], and sulphates[10] is also used. The detection limit of elements such as Pb, Nb, Ta, and W in steels and alloys is ~0.002%.[6,10]

The XRF analysis of the precipitates obtained is carried out using an external standard, and the reference specimens are prepared as the same precipitates. In addition to external standards, internal standards can also be used. Thus in the determination of U, Np, Pu, and Am,[7] the internal standards added to the solution are Y and Sc, which are then precipitated together with the other elements using NH_4OH.

Uranium has been determined[11] at the 10^{-4}% level after precipitating as barium diuranate; the precipitate was sorbed not on the polycarbonate membrane usually employed, but on an Ag membrane filter. This lowered considerably the minimum quantity of uranium detectable, as a result of the excitation of the fluorescent emission of uranium not only by the primary radiation of the X-ray tube but also by the secondary emission from the silver support.

Precipitation is being used successfully to determine not only heavy metals but also various light elements. Thus phosphorus can be determined in purified copper at the level of 5×10^{-4}% in a 5 g specimen with preliminary precipitation of phosphorus by ammonium molybdate[8]. The quantity of phosphorus can be determined from the fluorescent emission of phosphorus and molybdenum. The determination of parts per million of chlorides in various silver catalyst specimens has been described[12]. Good results can be achieved by coprecipitating traces of elements with iron[13,14] and cobalt[15] hydroxides; the method described above is used to prepare the emitters.

2. The Use of Organic Precipitants

Most of the work based on a combination of precipitation with the XRF determination of elements has been carried out using organic precipitants[16]. Mention must first be made of those studies where heavy metals have been precipitated using sodium and ammonium carbamates.

Thus sodium diethyldithiocarbamate has been used to determine traces of Cu, Zn, Hg, and Fe in salt solutions[17,18] and of Cu, Zn, Cd, and Pb in aqueous solutions[8], to determine the principal components of Mn,Zn- and Ni,Zn,Co-ferrites[19], in the multi-element analysis of sedimentary and other rocks[20], and to determine low concentrations of Mn and Fe in titanium[21]. Kessler and co-workers[22,23] used titanium diethyldithiocarbamate to coprecipitate traces of transition metals. Japanese workers have determined traces of Cu, Zn, Fe, and Ni in pure aluminium and magnesium by precipitating with ammonium pyrrolidine-1-dithiocarbamate; the XRF analysis of the precipitate was carried out using an external standard. For this purpose, selenium was added as internal standard to the solution[24]. The concentrations of Fe, Co, Cu, Zn, Cd, and Pb in water at the 10^{-9}% level were determined by coprecipitating these metals with Mo pyrrolidinethiocarbamate complex carrier[25]. Cr, Cu, Zn, As, and Se in water at the 10^{-7}% level was determined similarly, except that the carrier used to coprecipitate these elements was the Fe pyrrolidinedithiocarbamate complex[26].

Methods have also been described for determining heavy metals by coprecipitating with polyvinylpyrrolidone and thionalide[27], by precipitating as salts of glycollic acid[28], and by coprecipitating Co and Ni with iron hydroxide using hexamethylenetetramine[29].

Traces of tungsten in iron, molybdenum, and titanium have been determined by precipitating the tungsten with phenylfluorone solution after dissolving the metal specimen[30]. A method has also been proposed for the simultaneous XRF determination of Nb, Zn, and Ta at the 10^{-2}% level after precipitating with phenylarsonic acid[31]. It has been shown possible to determine transition metals after precipitating them with 1-(2-pyridylazo)-2-naphthol[32]. Standard XRF methods for determining Fe at the 10^{-4}% level include its determination after precipitating with 1-(2-pyridylazo)-2-naphthol[33].

In the determination of traces of Al, Fe, and Ti in different gypsum specimens, the metals were precipitated by Cupferron from acidic solutions (pH 3.5–3.7) after dissolving the gypsum by fusing with H_3BO_3 and Na_2CO_3 followed by solution in H_2SO_4.[82] This method gives good reproducibility, the coefficient of variation does not exceed 2.6%, and the minimum detectable quantities of Al, Fe, and Ti are 0.15, 0.58, and 0.15 μg respectively.

Sometimes, not one but several precipitants are used to precipitate micro-quantities of metals. In those cases where both precipitants are organic reagents, however, multiple precipitation may not take place, since the first precipitant forms complexes and prevents the precipitation of some elements by the second precipitant. This effect can be observed when Cupferron and phenylfluorone are used in succession. On the other hand, a successful combination of reagents gives good results.

Thus traces of Mn, Fe, Ni, Cu, Zn, Cd, Sm, Hg, and Pb have been coprecipitated from solutions using a mixture of 1,10-phenanthroline and sodium tetraphenylborate in the ratio 1:1.[34] Tetraphenylborate is also used to precipitate K and Rb.[20,35] In all the procedures described, the precipitates were filtered through microporous membranes or compact filters, and the specimens obtained in this way were studied by XRF spectrometry. A special apparatus has been developed for the selective electrodeposition of Ni, Cu, and Zn, and the XRF analysis of the deposit[36].

Thus the combination of precipitation and XRF determination is rapid, sensitive, accurate, and, which is most important, universal. It is necessary, however, to remember the possible errors, associated with incomplete precipitation of the elements to be determined or the coprecipitation of elements which interfere with one another in the XRF determination, and also the marked difference between the actual and theoretical density of the precipitate. Examples of the combination of XRF with precipitation are given in Table 1.

Table 1. Examples of combined XRF analysis and precipitation.

No.	Precipitant	Material	Elements determined	Refs.
1	Sodium diethyldithiocarbamate	salt solutions	Cu, Zn, Hg, Fe^{3+} (0,01—10 mg litre^{-1})	[17, 18]
2	ditto	water, pH 5.5	Cu, Zn, Cd, Pd	[8]
3	»	ferrites	Mn, Zn, Ni, Co, Fe (~ 5 μg)	[19]
4	»	water, pH 8.0–8.2	transition metals	[22, 23]
5	»	titanium, pH 7–9	Mn, Fe (50–100 μg)	[21]
6	»	ores and sedimentary rocks	Ti, Mn, Fe, Ni, Cu Zn, Pb, As, Sr	[20]
7	Ammonium molybdate	purified copper	P ($3 \cdot 10^{-4}$%)	[8]
8	$La(NO_3)_3 + NH_4OH$	crude copper	As, Bi, Fe, Pb, Sb, Te, Sn	[8]
9	*	solutions	Ni, Cu, Zn ($1 \cdot 10^{-100}$%)	[36]
10	Sodium tetraphenylborate	water	K (0.1–1000 μg)	[35]
11	1,10-Phenanthroline + Na tetraphenylborate (1:1)	water, pH 4–6	Mn, Fe, Ni, Cu, Zn, Cd, Sn, Hg, Pb, Co	[34]
12	1-(2-Pyridylazo)-2-naphthol	water, pH 10	Cu, Zn, Fe, Co, Ni (0,1—0.5 μg in 50 ml)	[32]
13	Pyridylazonaphthol	molybdenum, pH 10	Fe ($5,6 \cdot 10^{-4}$—$5 \cdot 10^{-3}$%)	[33]
14	Phenylarsonic acid	steel	Nb, Zr (0,01%)	[31]
15	Phenylfluorone	iron, 1% H_2SO_4 solution		[30]
16	Glycollic acid	organic material, water, pH 4.7–5.0	Hg, Ni, Pb, Se, As, Cd, Cu, Fe, Zn ($5 \cdot 10^{-6}$—$2,5 \cdot 10^{-5}$%)	[28]
17	Polyvinylpyrrolidone-thionalide	water, pH 4	Sn, Te, Hg, Pb (30—600 μg litre^{-1})	[27]
18	Ammonium pyrrolidinedithiocarbamate	water, pH 4	Cr, Cu, Zn, As, Se (10^{-7}%)	[26]
19	ditto	water	Fe, Co, Cu, Zn, Pb (10^{-9}%)	[25]
20	»	water	Cu, Zn, Fe, Ni, Mg, Al (< 50 μg)	[24]
21	NH_4OH	RuO_2	Th (0,1—1,2%)	[9]
22	ditto	water	U, Np, Pu, Am (0.05 μg)	[7]
23	»	Cu (metal), pH 9–10, Fe^{3+} ions	Bi	[14]
24	»	pH 8.5, Fe^{3+} ions	Zn, Cu, Pb, Mn (10—75 μg)	[13]
25	Na_2S	aluminium	Fe, Mn, Zn, Cu (10^{-4}%)	[4]
26	ZnS+MnS	water	Hg, Ag, Cu, Bi, Pb, Cd, Sn, As, Se, Tl, Zn, Co, Ni	[5]
27	H_2SO_4	steel, Ba^{2+} ions	Pb (0,02—0,5%)	[10]
28	H_2SO_3	Fe alloys	Nb, Ta, W ($2 \cdot 10^{-3}$%)	[6]
29	NaOH	molybdenum	Zr, Ti (10^{-8}—10^{-7} r)	[15]
30	Cupferron	gypsum, pH 3.5–3.7	Fe, Al, Ti	[82]
31	8-Quinolinol	water, activated carbon	heavy metals	[38]
32	8-Quinolinol	water, pH 8, activated carbon	ditto	[39]

*Electrodeposition.

III. X-RAY FLUORESCENCE ANALYSIS COMBINED WITH ION EXCHANGE AND SORPTION

In 1977, Leyden[37] reviewed XRF methods for determining metal ions in water specimens with preliminary concentration[37]. The most promising methods of concentration were sorption methods, particularly those using special filters and membranes with immobilised ionogenic groups. All the work reviewed[37] can be divided into two groups. The first involved the sorption of the metals or their complexes on activated carbon, or ion-exchange concentration on a resin. The concentrates obtained were generally subjected to further treatment to obtain an emitter convenient for XRF. The second group involved the use of ion-exchange membranes and paper, and in this case the concentrate was obtained in a form suitable for the XRF determination of the elements.

1. The Use of Ion Exchange Resins and Activated Carbon

The sorption of metal chelates on activated carbon is well known. This property has been used by a number of workers to concentrate heavy metal oxinates on activated carbon with subsequent XRF determination of the metals in the concentrate[38–40,80]. The authors cited not only developed a quantitative method for determining Mn, Fe, Co, Ni, Cu, Zn, and Al in waters of different types but also found the quantitative characteristics of the dependence of the distribution of the complexes of these elements with 8-quinolinol on various factors (pH, reagent concentration, metal concentration, etc., and also the presence of large quantities of alkali and alkaline earth metal ions in the solution).

Transition metals are often concentrated using the commercially available ion exchanger Chelex-100 (a complexing ion-exchange resin of the ketoimine–carboxylate type). This resin has been used to determine uranium in ground water[41]. A weighed specimen of the resin was placed in a previously acidified solution of the water being analysed, after which the resin with the sorbed uranium was filtered off on a membrane filter, dried, and compressed with a binding agent (Somarmix) on a boric acid support. The disc obtained in this way was used for the XRF analysis; the uranium detection limit was 2×10^{-7}%. Ca^{2+}, Ti^{3+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, As^{3+}, and Br^- were determined similarly in solutions containing these elements at concentrations of 5×10^{-6} to 5×10^{-4}%.[42]

In some cases, however, a dynamic method of ion-exchange concentration is more convenient. For example, Cu and Ni have been determined at the 0.5–5 μg litre^{-1} level, and Zn at the 4–15 μg litre^{-1} level in sea water[43]. The sea water was passed through a column of resin, after which the resin with the sorbed ions was compressed to form a disc. The minimum detectable quantities of Cu, Ni, and Zn are 0.3, 0.1, and 0.1 μg litre^{-1} respectively. A similar method has been used[44] to determine traces of a number of elements in various materials.

An interesting method for determining lead and mercury[45] using diethyldithiocarbamate on a support of Chromosorb W-DMCS gives 100% concentration. The detection limits for cadmium and mercury are 0.08 μg and 1.7 μg respectively[45].

Several papers in this field have been published in the Soviet literature. An X-ray–radiometric method, combined with ion-exchange concentration, has been used to determine noble metals (gold, rhenium, and silver);[49] the detection limit was 0.1–0.01 mg litre^{-1}. In the determination of Cu, Zn, Cd, and Pb in sewage[81], the metals were concentrated using the strongly acidic monofunctional KU2×8 cation exchange resin.

Amberlite IRA-400 in the Cl form has been used to determine low concentrations of uranium [$(0.2–5) \times 10^{-4}$%] in carbonate–bicarbonate solutions. To prepare the emitter, the resin with the sorbed uranium was filtered off and distributed in a uniform layer on a Mylar film fixed in a special holder[48].

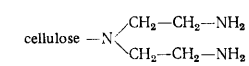
In the development of this trend in XRF, research workers are now using new and more selective sorbents. Japanese workers have developed a method for determining microgram quantities of metals by XRF combined with extraction from solutions by chelating functional groups immobilised on SiO_2.[47] A whole series of new sorbents have been prepared and studied in detail, together with the conditions for the extraction of Hg, Cu, Zn, Ni, Pb, Eu, and Mn as the preliminary concentration stage in XRF analysis[80]. A disadvantage of sorbents of this type is their instability in concentrated acids and alkalies.

Substituted cellulose powder containing 1-(2-hydroxyphenylazo)-2-naphthol or 4-(2-pyridylazo)resorcinol groups has also been proposed for concentrating metals in XRF analysis[45]. The combination of ion-exchange concentration on a column and XRF determination of the elements in the resin phase is not very convenient, however, since the preparation of a suitable emitter for XRF spectrometry is very tedious, and introduces additional errors, and the use of loose resin specimens for spectrometry lowers considerably the sensitivity of the determination and the accuracy of the analysis, as a result of the increase in the standard deviation, associated with the nonuniformity of the particles.

2. The Use of Ion Exchange Papers and Membranes

In XRF analysis, increasing use is now being made of analysis by a thin layer technique, since it makes it possible to avoid matrix effects. Work in which elements are concentrated using paper impregnated with an ion-exchange resin, and different types of filters containing complex-forming groups, is therefore of considerable interest.

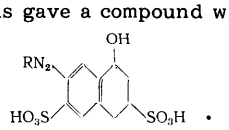
A method of obtaining filters of this kind, capable of concentrating transition and alkaline earth metals, has been described[50]. Chlorodihydroxycellulose (obtained by the reaction of $POCl_3$ with Whatman-41 cellulose) was treated with diethylenetriamine or iminodiacetonitrile, followed by reduction. This gave a chelating ion-exchange filter:



which was used successfully in XRF analysis.

Filters of this type are also available commercially, for example Chelex-100 and Acropore-SN, with diameter 47 mm, containing chelating iminodiacetic acid groups[51]. Thus uranium in ground water has been determined using Chelex-100 [52] and Whatman R-81 [53] filters, and also a filter containing 20% SiO_2, modified by silylation with N-β-ethylaminopropyltrimethoxysilane[54]. The uranium detection limit reached 0.3 μg.

Traces (2.5 ppm.) of Fe, Cu, Zn, Sr, and Hg have been isolated from water using specially prepared cellulose filters[55]. The chromotropic functional group was introduced into the cellulose as follows: *p*-aminophenylcellulose (RNH_2) was first prepared, after which RNH_2 was treated with a mixture of HCl and $NaNO_2$ to give $RN_2^+Cl^-$, to which chromotropic acid was added. This gave a compound with a capacity of 0.2 mmole g^{-1}:



As already noted, ion-exchange filters are being used increasingly in XRF analysis. The number of studies in this field has increased sharply in recent years. The method is used in the analysis of water and in the analysis of various organic and inorganic materials after decomposition. One of the most interesting studies describes the determination of calcium and strontium in mineral waters[56]. The mineral water was passed eight times through a Whatman SA-2 filter impregnated with a cation exchange resin. The XRF spectrum was excited using the ^{109}Cd isotope. The detection limit according to the 3σ criterion is 7×10^{-5}–2×10^{-3}% for calcium, and 5×10^{-6}–2×10^{-4}% for strontium.

Traces of Cr, Fe, Cu, Zn, Sr, Cd, and Ba in surface waters have been determined using Amberlite NR-120 ion-exchange paper[57]. Similar methods have been used to determine Hg in water[58], osmium and ruthenium in the presence of large quantities of Cu, Fe, and Ni[59], the lanthanides[60], gold and silver in metallic copper[61], V, Cu, Fe, and Ni in mineral oils[62], and a number of other elements[63]. It should not be concluded, however, that the combination of ion-exchange separation on a filter with an XRF determination is suitable only for determining cations. The method has been used for the quantitative determination of sulphates[64]; the solution is passed through a filter of SB-2 anion-exchange resin, with subsequent XRF determination of sulphur.

The methodology of a study of the determination of copper and silver in pure lead[65] differs from that of the above studies. To separate Pb, the dissolved specimen is passed through a column of Chromosorb W-HP impregnated with a solution of dithizone in *o*-dichlorobenzene, and the silver and copper ions remaining in solution are concentrated on 2.5 cm diameter discs of SERVA-SB-2 ion-exchange paper as the complexes $[AgI_4]^{3-}$ and $[CuI_4]^{2-}$. Silver and copper are determined by XRF.

Table 2. The use of ion-exchange filters and membranes for preliminary concentration in XRF analysis.

No.	Filter	Material	Elements determined	Refs.
1	Chelex-100	water, pH 7–8	heavy metals	[51]
2	Chelex-100	water	U ($0{,}5 \cdot 10^{-7}$%)	[52]
3	Chelex-100	water, pH 2.5	U (0.3 μg)	[53]
4	Paper impregnated with $AgNO_3$	steel	Se (10 μg)	[66]
5	SB-2	lead	Ag, Cu (0.2 μg)	[65]
6	SB-2	fuel	SO_4^{2-} (1%)	[64]
7	SB-2	water, pH 0.3	Os, Ru	[59]
8	SB-2	water	Hg (1 μg in 50 ml)	[58]
9	Chromatographic paper	water	Cs, Ba, Ln, Ag, Zn, Fe, Hg (10^{-7} g)	[63]
10	Ion-exchange membrane	mineral oils	V, Cu, Fe, Ni (10^{-4}%)	[62]
11	Ion-exchange membrane	copper	Au, Ag (100 μg)	[61]
12	SA-2	metals	Ln (10 μg)	[60]
13	Amberlite HP-120	water	Cr, Fe, Cu, Zn, Sr, Cd, Ba (1–$3 \cdot 10^{-4}$%)	[57]
14	SA-2	water	Ca ($7 \cdot 10^{-5}$%), Sr ($5 \cdot 10^{-7}$%)	[56]
15	Cellulose with the chromotropic group	water pH 4–7	heavy metals (1×10^{-5}%)	[55]
16	Cellulose with amino-groups	water	Ln	[50]

Paper can be impregnated not only with an ion-exchange resin but also simply with solutions capable of absorbing substances liberated as gaseous products. Thus Japanese workers have proposed a method for determining selenium in steels, based on its liberation as H_2Se and fixing on paper impregnated with silver nitrate[66]. When the liberation of H_2Se was complete, the paper was used as the emitter in the XRF determination (see Table 2).

Although the use of ion-exchange filters and membranes is attractive, they generally have a low capacity, which is inconvenient in the analysis of solutions with a large salt background.

IV. COMBINATION OF X-RAY FLUORESCENCE ANALYSIS WITH EXTRACTION

The combination of the XRF determination with concentration by extraction is of interest, because of the speed and simplicity of the extraction concentration. Both liquid extraction and extraction by low-melting organic substances are now used.

1. Liquid Extraction

One of the first studies in this field dealt with the determination of transition metals at concentrations of 10^{-8}–10^{-6}%.[67] The metals were extracted as the diethyldithiocarbamate complexes by carbon tetrachloride. Polystyrene was then added to the extract, and the mixture evaporated on a Mylar film under an infrared lamp. This film was then analysed by XRF.

Later, a more complex method of preparing the specimen was used to determine V, Cr, Mn, Fe, Co, Ni, Cu, and Zn in sea water[68]. The elements to be determined were separated as the pyrrolidinedithiocarbamates by treating with methyl isobutyl ketone, and then transferred to nitric acid solution and sorbed on cellulose powder, which was compressed to form a disc. The reference specimens were prepared similarly from standard solutions. The elements listed could be determined at concentrations of 0.1 μg litre^{-1}.

Micro-quantities of palladium in titanium alloys have been determined by extracting palladium diethyldithiocarbamate with chloroform[69]. The emitter was prepared by impregnating a 15 mm diameter filter-paper disc with the extract. A similar method was used to determine technetium in waste products from nuclear fuel production[70], and uranium and neptunium in metallic plutonium[71].

In the Soviet literature, the determination of micro-quantities of tantalum in technetium solutions[72] and of zirconium and hafnium in heat-resistant alloys[73] by a combination of liquid extraction and XRF determination of the metals in the extract has been described.

Leyden[74] determined phosphorus in natural waters at concentrations of 10^{-7}% using selective extraction by ethyl acetate as molybdophosphoric acid. Phosphorus was determined using the Mo K_α line. This indirect determination of light elements from the emission of heavier elements is opening up a new and promising field in the XRF analysis of light elements.

2. Extraction by Low-Melting Organic Substances

Increasing use is now being made of low-melting organic extracting agents, and solutions of extracting agents in low-melting organic solvents. The combination of high-temperature extraction with XRF analysis of the extract is particularly promising, since when the extraction mixture is cooled, the solid organic phase is obtained directly in a form suitable for spectrometry. This property has been used in the determination of Cr, Fe, Co, Ni, and Cu in fresh water after extraction by molten 8-quinolinol at 98 °C.[75]

One of the most widely used low-melting solvents is naphthalene[76] or its mixtures with other organic substances[77]. The use of naphthalene as extracting agent, however, does

not make it possible to determine elements whose XRF analysis requires a vacuum. Another disadvantage of working with naphthalene is the low viscosity of its solutions, which causes difficulty in the separation of phases with markedly different quantities. It is much more convenient to use as the organic phase a mixture of C_{17}–C_{20} aliphatic acids.

Micro-quantities of Cr, Mn, Fe, Co, Ni, Cu, and Zn have been extracted by a solution of 1-phenyl-3-methyl-4-benzoylpyrazolone-5 in a molten mixture of aliphatic acids[78]. A similar procedure has been used[79] to determine bismuth in various materials with preliminary extraction by dithizone or 2,3,4-trihydroxy-4'-chlorobenzene (sic). Japanese workers have concentrated Co, Fe, Ni, Cu, Zn, Pb, Bi, and Cd by extracting their pyrrolidinedithiocarbamate complexes into molten stearyl alcohol[83]. The chelates of all these metals except iron are transferred quantitatively to the organic phase at pH 5. The extraction of iron is not complete, since its chelates are unstable at high temperatures.

Extraction by low-melting organic substances provides an approach to the solution of the problem of the standardisation and unification of the XRF determination of traces of elements in various natural and industrial materials. The combination of the individual solution of the specimen to be analysed with subsequent extraction by low-melting organic substances and the production of an emitter from the solidified extract makes it possible to obtain a standardised matrix which is independent of the previous history of the substance being determined.

The general questions of the metrology of chemical XRF analysis have been examined in detail[84]. An analysis of the dependence of the relative standard deviation $S_{r,\,c}$ on the concentration $c_{min,\,p}$ showed that preliminary concentration makes it possible not only to lower $c_{min,\,p}$ but also to increase the reproducibility of the results at low concentrations. The use of low-melting extracting agents makes it possible to lower the random and systematic errors in the analysis by eliminating matrix effects and making possible the construction of universal calibration characteristics. If the low-melting extracting agent contains only light atoms, it is possible to reduce to a minimum the effects of absorption and selective excitation. On the other hand, if it is necessary to produce very thin saturated layers, it is possible to use low-melting extracting agents containing heavy atoms, for example bromine. The use of hetero-organic compounds with a known concentration of the reference element makes it possible to increase considerably the accuracy of the determination using an internal standard.

It should be emphasised again that chemical XRF analysis is finding increasing application in the analysis of water and in the analysis of other most varied materials (steels, alloys, and organic and biological materials). In the analysis of solid substances, concentration is preceded by solution.

The choice of the optimum method of concentration is determined by the conditions of the analysis, interfering elements, and the accuracy and sensitivity required in each specific case.

As already noted, an advantage of the methods described, compared with traditional non-destructive XRF methods, is that the preliminary decomposition and concentration of the specimen makes it possible to eliminate the corrections for matrix effects and non-uniformity of composition and particle size. On the other hand, the combination of chemical methods of concentration with the XRF determination of elements in the concentrates makes it possible to avoid the restrictions associated with the chemical nature of the elements being determined (the superposition of colours in photometry, etc.), and does not require preliminary separation of the elements.

Thus the combination of XRF with various chemical and physicochemical methods of concentration is a promising development in the determination of traces of elements.

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