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Total reflection X-Ray fluorescence analysis and application in biological system and textile industry

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ABSTRACT

Total reflection X-ray fluorescence (TXRF) spectroscopy is developed in recent 20 years and has been used for the determination of trace metal ions in various media such as water samples, geological samples etc. For the simultaneous determination of elements with atomic number greater than 11 in various matrices, TXRF is a universal and economic method. Today, TXRF as a micro trace element analysis technique takes place between the other spectroscopic techniques.

In the present study, the determination of antimony, arsenic, lead, cadmium, chromium, cobalt, copper, nickel, mercury and zinc in the cloth samples produced in Kayseri-Turkey have been performed after extraction with artificial sweat solution and decomposition with nitric acid. TXRF technique is suitable for the determination of 7 trace elements, in the sweat extract and decompose solution except mercury and cadmium. In addition, it was observed that the element contents of textile samples are different from each other as ‘finger print type, TXRF-spectrum. This technique can also be used for the identification of textile sample in criminal investigation.

INTRODUCTION

In last years, the environmental sensitivity and the efforts for the protection of health against to environmental objects (i.e. by using environmentally friend products and productions) were increased significantly. On the other hand, detection of trace amount of materials and micro- or nanoanalysis are possible with the modern analytical techniques developed in last years. Therefore, today it is possible to detect the very low amount of hazardous material against to the health[1-3].

Textile producers and related associations as well as research and testing institutes took this as a good opportunity for a new market segment and created so-called eco-textiles. They are specially labeled as toxicologically tested. Especially the European Countries are very sensitive for the hazardous materials such as allergic or carcinogen chemicals including trace heavy metal ions originated from clothing textiles[4-6]. Hence, these countries are evaluated carefully the imported textiles from the other countries such as Turkey.

Toxic and allergic metallic elements including antimony, arsenic, lead, cadmium, chromium, cobalt, copper, nickel, mercury and zinc, formaldehyde and chlorinated hydrocarbons can be exist in natural structure of textiles or they can be penetrated into the textile during the production, dying or via the protection agents in storage of the textiles. The most important standard in Europe for Textiles is Oko-Tex Standard 100. The levels of extractable metals with artificial sweat in Oko-Tex Standard 100 has been re-arranged at March 2000. The limit levels for heavy metal contents of textile products before and after March 2000 are given in Table 1 and Table 2, respectively. Before March 2000, antimony was not listed in Oko-Tex Standard 100 and zinc was in the list. Also the concentration levels of the other metal ions in the list was changed by OKO-TEX.

Table 1. Limit values of extractable heavy metals at 1999 (mg/Kg textile)[6].

Elements	For Baby	For Adult
Arsenic	0.02	0.2
Lead	0.08	0.8
Cadmium	0.1	0.1
Chromium (total)	1	2
Cobalt	1	4
Copper	5	25
Nickel	1	4
Mercury	0.02	0.02
Zinc	10	50
Antimony	-	-

- : No values given

Table 2. Limit values of extractable heavy metals at March 2000 (mg/Kg textile)[7].

Elements	For Baby	In direct contact with skin	With no direct contact with skin	Decoration materials
Arsenic	0.2	1.0	1.0	1.0
Lead	0.2	1.0	1.0 *	1.0 *
Cadmium	0.1	0.1	0.1 *	0.1 *
Chromium	1.0	2.0	2.0	2.0
Cobalt	1.0	4.0	4.0	4.0
Copper	25.0 *	50.0 *	50.0 *	50.0 *
Nickel	1.0	4.0	4.0	4.0
Mercury	0.02	0.02	0.02	0.02
Antimony	5.0	10.0	10.0	10.0
Zinc	-	-	-	-

* No requirement accessories made from inorganic materials.

- Total pesticides 0.5 for Baby and others 1.0 mg/Kg

- : No values given

Various studies have been performed for the determination of some trace metal contents of the textile products. Zinc and copper contents of tenth cloth produced in India have been determined with flame atomic absorption spectrometry (FAAS) and/or inductively coupled plasma atomic emission spectroscopy (ICP-AES) by Raghunath et al.[8] after selective dissolution of zinc and copper naphthenates into EDTA. The determination of iron on cloth has been performed with wavelength-dispersive x-ray fluorescence spectrometry by van Dalen[9]. Koizumi and Suzuki[10] have been proposed a procedure for the determination of total cations and anions of thee wiping cloths. Prange and co-workers[11] have been analysed various fibers of different textile material including polyesters, viscose and wool by total reflection X-ray fluorescence spectrometry. Metal contents of cotton samples have been determined wit atomic absorption spectrometry by Brushwood and Perkins[12]. For the determination of iron contents of cotton yarn and fabric, woolen fabric, a spectrophotometric method has been proposed by Grabaric et al.[13].

Total reflection X-ray fluorescence (TXRF) Spectroscopy[14-15]

Total reflection X-ray fluorescence (TXRF) spectroscopy which is a special modification of energy dispersive X-ray fluorescence (ED-XRF) spectroscopy has gained very big importance for the determination of elements with the atomic number of larger than 11 in last two decades. In this new design; the sample is placed over the specific sample holder containing smooth surface and a reflector. The beams emitted from X-rays tube are felt over the sample holder with very small angle (1-4 min), therefore almost all of the beams are reflected. Only the sample atoms from the sample holder and emitted fluorescence beams can be reached to the energy dispersive detector which placed in a vertical position according to the sample holder. Hence, the determination capacity of the system is increased 100-1000 times according to the classical XRF technique. In addition, it is possible to place a few μl solution or a few mg solid sample over the sample holder, therefore this technique can be used both in microanalysis and trace analysis.

Methods of X-Ray Fluorescence. The sample or the objet of interest is first irradiated by means of an x-ray tube, producing a broad x-ray beams with a cylindrical shape. The primary x-ray beam excites the sample and as a reaction, the atoms in it emit a secondary x-ray beam, the fluorescence signal. The fluorescence radiation detected by an x-ray spectrometer, with collimators, Bragg crystal and x-ray detector, and recorded an x-ray spectrum. The spectrum processed with a computer, wavelength and intensity of all spectral lines are determined and elemental composition of the sample is calculated.

Several x-ray tubes are used for excitation of the samples. These are operated at high voltage up to 100 kV (mainly up to 60 kV) while the current is adjusted to a maximum power of 2-3 kW. The classic spectrometer called wavelength dispersive. These consists of a goniometer with a rotating Bragg crystal, gas-flow or scintillation detector. Total spectrum is recorded sequentially within about 1 hour.

After 1960 were developed special semiconductors, and energy dipersive spectrometer was built. These type spectrometer don’t need a rotating Bragg crystal and a goniometer. These work only with a high sophisticated solid state detector like Si (Li), record a total x-ray spectrum simultaneously within a few seconds. All type of sample, conducting and isolating solids, powdered materials, liquids and gases can be subjected to x-ray fluorescence. These called energy dispersive x-ray fluorescence analysis (ED-XRF).

All elements in periodic system without H and He can be analysed qualitative and quantitative by XRF. Because the frequencies of characteristic x-ray lines proportional to the atomic number of elements and the number of photons detected as intensity of the lines is generally proportional to the concentration of the corresponding elements in the samples. A variety of samples can be analysed without sample preparation. However quantitative results are unfortunately effected physical and chemical matrix effect. The heavy metals like Ti, V, Cr, Co, Ni, Cu, Zn, Se, Cd, Pb and U can be determined in a range from 100 percent up to 1-10 ng/kg by TXRF.

The instrumentation of TXRF is relatively simple in comparison with that of other modern methods of spectroscopy. An excitation unit containing a high voltage generator and a X-ray tube a total reflection module and a detection unit with semiconductor detector and a multi channel analyser are needed. The operation and the study also the preparation and the enthusing of sample is fairly simple and operation costs are reasonable.

TXRF differs from conventional ED-XRF mainly in the excitation geometry. A flat primary x-ray beam is generated by a high power x-ray tube (Mo or W) with a line focus, is filtered by a thin metal foil and sheet like shaped a pair of precisely aligned slits. The polychromatic beam is deflected by a first reflector with may be a simple quartz glass mirror. The primary spectrum is simplified and more and less monochromatized. After passing the first reflector primary beam hits the sample- carrier as a second reflector under grazing incidence. It is totally reflected. It is totally reflected within the sample are effectively excited. It is totally reflected here under glancing angle of only 0.1 degree. If loaded with some amount of sample material the atoms within the sample effectively excited to x-ray fluorescence.

Comparison of TXRF with other methods of Atomic spectroscopy. The detection limits for most methods being suitable for trace analysis on elements are well-known. The TXRF method has a low limits of detection for most of elements than other spectroscopic methods. With regard to the isolated elements, TXRF can reach or even surpass the capability of other more common methods, e.g. ICP-OES, NAA or ETAAS.

The methods of AAS is the most common method of atomic spectroscopy. Only this techniques involving electrothermal atomization (ETAAS) show detection limits comparable to those of TXRF. Sample quantities for the analysis of solutions and solids are at ml and upper μg-levels respectively. Consequently, ETAAS is also regarded as a micro-method. At present, only a single-element detection is possible, although, simultaneous multi-element detection is envisaged for laser AAS. A further disadvantage of AAS is the necessary atomization process presenting a source of systematic errors that can only be minimized by various tricky operations.

In last 20 years, TXRF is used for the determination of toxic trace elements in very different type of medium and matrices such as water, sea water, wastewater, mineral and spring waters, biological tissue, blood, fuel oil, antique picture paints, fuel oil, airborne, sludge etc [16-28].

In this study; possibility of the simultaneous determination of toxic and allergic trace elements contained by different types of textiles in a very short time was investigated by TXRF which is simple, rapid, ecofriendly and cost effective technique for the determination of trace metal contents of the samples.

EXPERIMENTAL

Apparatus

The instrument used was a commercially total reflection X-ray fluorescence spectrometer (EXTRA II, Rich, Seifert & Co, Ahrensburg, Germany) equipped with a Si (Li) detector, electronics and multi channel analyzer (system QX 2000, Link Systems Oxford Instruments, UK.). The X-ray tube with a Mo target was set at 58 kV and 10-30 mA. Measuring time was 1000 s. Yttrium was used as internal standard. The samples on the siliconized quartz-glass carriers were pipeted. After drying the solution the residue was analysed by TXRF. A high pressure asher (HPA, Kürner, Rosenheim, Germany) with 70 mL quartz-glass vessels was used for the decomposition of the textile samples.

Reagents

Otherwise stated, all chemicals obtained from commercial sources were of analytical grade and suprapure grade for TXRF measurements. All aqueous solutions were prepared from doubled-quartz-distilled water. Artificial acidic perspiration solution was prepared according to ISO 105-E-04 [29]. 0.5 g L-histidine monohydrochloride, 5.0 g NaCl and 2.2 g disodium hydrogen ortophosphate were dissolved in water. The solution was brought pH 5.5 with 0.1 M NaOH. The solution was prepared daily.

Procedure for the cloth samples

The cloth samples collected from the various textile plants in Kayseri-Turkey. Two different procedure were applied to the cloth samples:

a- Extractable Metal Levels: In order to determine extractable metal levels, the cloth textile samples were extracted with artificial acidic sweat solution. For this purpose 0.5 g of each cloth was weighed and transferred to 25 ml beaker. Then 10 ml of artificial perspiration solution was added. The solution was heated at room temparature for 24 hours on a magnetic stirrer. Then, the cloth sample was separated to the solution. The volume of the final solution was completed to 10 ml in a volumetric flask. The element concentration in the final solution were determined by TXRF.

b- Metal Contents of Cloth Samples: To determine total metal contents of the cloth samples, 0.2-0.5 g of cloth textile samples were weighted and digestion agent was used nitric acid in a high pressure asher. The pressure and temperature in the digestion procedure were 13000 kPa and 280 °C, respectively during a period of 1h. After decomposition of textile samples, the metal contents were determined by TXRF.

For TXRF measurements, 990 µl of a sample was pipetted into a small vessel and 10 µl of 1 mg/ml yttrium as internal standard was added. 30 µl of this solution was transferred onto a quartz sample support and dried under a IR-lamp for 10 min. Then the sample was analyzed by TXRF.

RESULTS AND DISCUSSION

TXRF is suitable techniques for the simultaneous determination of the elements with the atomic number of larger than 11. The amount of Cr, Co, Ni, Cu, Zn, Cd, As, Sb, Hg, Pb which are required elements in the ÖKO-TEX 100 standard, after their extraction into the artificial sweat and after decomposition by nitric acid were investigated by TXRF for 25 types of clothing textiles produced in Kayseri-Turkey. The results were compared with the standard values. The results of the determination of same heavy metals in artificial sweat extract are given in Table 3. It was obtained that 8 elements (out of Hg and Cd) can be determined easily and in a very short time both in textiles and in artificial sweat by TXRF. The limit values for Hg and Cd are lower than the detection limit of TXRF. The chromium and arsenic contents in the sweat extract were found to be at very low levels and also below the detection limit for the lots of the textile samples. The antimony contents of the all samples were at very low levels, but antimony can be easily determined in textile samples by TXRF. The limit level of antimony in the ÖKO-TEX standard 100 is 10 mg/Kg.

The result of determination of the same elements in direct digested textile are given in Table 4. The results for addition elements such as P, Ca, Ti, V, Mn, Fe, Sr and Ba only after direct digestion of textile materials with nitric acid are given in Table 5. The element contents of textile samples are different from each other as ‘finger print type, TXRF-spectrum

Table 3. Results of the determination of some heavy toxic elements in artificial sweat extract of textile by TXRF spectrometry

	Element (mg/kg)						
Sample	Cr	Co	Ni	Cu	Zn	As	Pb
A	0.22	0.04	0.98	0.28	2.22	*	0.34
B	*	0.16	0.24	0.04	0.92	*	1.08
C	*	0.16	1.14	0.02	2.64	*	0.38
D	*	0.28	0.24	0.56	2.16	0.10	0.54
E	*	0.18	1.30	0.72	308	*	0.18
F	*	0.12	0.34	*	0.34	*	*
G	*	0.04	0.74	*	34.2	*	*
H	1.12	0.96	1.32	0.28	*	1.52	6.0
I	*	*	0.08	0.02	*	*	2.0
J	0.28	0.06	0.26	0.18	1.92	0.02	0.9
L	0.44	0.94	1.52	0.84	0.42	0.01	4.9
M	0.62	0.32	0.52	0.34	0.98	0.26	0.18
N	0.20	0.16	0.64	0.28	0.22	*	2.4
O	0.44	0.18	0.68	0.02	1.18	*	2.8
P	0.20	0.14	0.76	0.04	4.32	*	1.04
Q	*	0.12	0.26	0.32	0.14	0.02	2.5
R	*	0.06	*	*	1.46	*	*
S	*	0.02	0.10	9.90	2.26	*	*
T	*	0.04	0.36	0.36	4.96	*	0.36
U	*	0.01	0.16	13.58	1.48	*	0.9
V	0.9	0.06	0.30	0.12	3.46	*	0.4
X	*	0.16	0.44	0.54	2.74	0.10	0.5
Y	*	0.04	0.36	0.38	0.62	*	0.6
Z	0.42	0.08	0.2	0.34	4.04	0.10	0.05

* No detectable

Table 4. Quantitative results of the determination of 7 elements in textile after digestion with nitric acid in a high pressure asher (HPA).

	Elements mg/Kg, textile						
Sample	Cr	Co	Ni	Cu	Zn	As	Pb
A	0.64	*	0.32	0.37	3.74	0.30	0.46
D	0.50	0.11	0.45	0.95	2.30	0.09	0.24
E	1.07	0.37	2.23	36.3	955	0.25	0.48
B	1.37	0.11	0.92	0.41	2.48	*	0.51
G	3.13	0.38	1.27	2.16	437	0.15	0.23
H	56.6	15.9	0.78	0.70	2.21	0.12	0.51
I	0.19	*	0.13	0.29	1.29	*	0.16
J	0.55	0.20	0.71	0.99	7.07	0.16	0.76
L	16.9	3.53	1.52	4.60	4.78	0.15	0.24
M	0.37	0.90	0.41	28.4	3.34	0.09	0.20
P	0.59	0.11	0.56	0.50	3.72	0.09	0.40
Q	0.83	0.26	0.59	2.24	29.7	0.22	7.62
R	0.47	0.34	0.42	55.0	2.16	0.25	0.40
T	263	8.08	0.47	4.86	44.6	0.19	0.39
U	1.15	0.18	0.87	113	13.5	0.18	4.61
V	0.83	0.32	0.08	0.81	11.2	*	3.30
Y	1.31	0.14	1.22	0.73	1.98	0.11	0.25
Z	0.78	0.12	0.31	0.96	10.4	0.20	2.90
Blank	0.0025	*	0.0014	0.0014	0.0013	0.0013	0.0020
Blank	0.0026	0.0013	0.0028	0.0065	0.0019	*	0.0022

* No detectable

As can be seen in Table 3 and Table 4, while the level of the some elements in the digested samples were at high levels such as chromium in the sample T (263 mg/Kg) and cobalt in the sample T (8.08 mg/Kg), the levels of these elements in the sweat extract were at low levels such as as chromium in the sample T (Below the detection limit) and cobalt in the sample T (0.04 mg/Kg). The same condition are shown for copper in the sample U (113 mg/Kg), E (36.3 mg/Kg), for zinc in the sample E (955 mg/Kg), G (437 mg/Kg) and for lead in the sample Q (7.62 mg/Kg), U (4.62 mg/Kg) in the direct digestion.

These results can be indicated that, even levels of the metal in the textile samples at high levels, the levels of the sweat extract can be at low levels. Also the kind and quality of the textile sample are important parameters for low levels of these elements in the sweat extract. In the best quality clothes for dressing such as sample T and R, the levels of metals in the direct digestion were found at high levels, in the sweat extract at low levels.

Table 5. Quantitative results of the determination of 10 elements that are non-interesting for ÖKO-TEX 100 standard in textile sample after digestion with nitric acid in a high pressure asher (HPA).

Element (mg/ Kg textile)										
Sample	P	S	K	Ca	Ti	V	Mn	Fe	Sr	Ba
6AX	1070	10410	31.9	1069	2.50	0.81	3.50	36.3	9.45	2.83
1-D	214	424	1604	477	1.32	0.44	2.39	22.5	5.01	1.58
1-D	192	423	1531	471	1.04	0.34	2.50	22.1	4.85	2.05
2-E	190	288	29.3	201	77.3	1.23	1.19	28.9	0.92	4.81
2-E	186	356	28.8	195	78.7	0.72	1.36	29.5	0.79	3.42
3-I	92.2	194	8.2	198	0.88	0.25	1.10	15.7	2.74	1.33
4-R	480	1405	163	751	1.24	*	1.34	15.2	8.65	2.10
5-V	90.3	368	22.8	215	2.07	0.46	0.32	33.1	1.15	2.41
7-P	143	290	42.1	159	32.5	0.32	46.4	14.3	0.66	2.91
8-J	151	991	33.0	141	3.22	*	0.59	31.3	0.56	1.17
9-T	114	9001	6.39	491	67.3	1.02	33.2	12.8	3.21	4.02
9-T	110	8995	6.42	496	66.7	0.65	32.3	12.6	2.52	3.24
10-Q	139	509	20.9	233	17.9	*	69.7	110	2.48	1.47
11-B	127	290	13.0	279	39.0	*	15.6	12.0	1.31	1.08
12-L	120	538	24.8	628	43.2	0.52	3.36	27.8	2.36	33.7
13-H	97.8	430	39.7	390	3.36	0.31	0.90	62.5	3.56	2.82
14-G	102	1146	30.1	587	61.3	*	3.15	26.8	2.80	5.36
15-M	167	899	109	641	35.7	0.29	1.13	19.9	1.21	6.12
16-Y	153	241	159	363	41.5	0.83	1.36	27.3	137	5.20
17-U	207	398	127	999	46.0	0.38	1.15	39.2	3.69	3.30
18-Z	97.6	116	21.3	430	29.4	*	76.2	13.7	1.38	5.63
19-Bl.	2.5	0.24	0.06	0.12	0.63	*	0.005	0.014	0.019	0.0015
20-Bl.	2.80	0.18	0.21	0.35	0.54	0.005	0.002	0.034	0.020	0.0016

The reproducibility study was also performed with a well-known cotton gabardine textile sample symbolized (I) in all tables. The reproducibility values for Fe, Ti were below 20 %, for Cu, Ca, Mn, Co, Cu, Zn, As, Pb and Ba, they were found in the range of 20-30 % and for Cr and Ni higher than 30%.

The determination of the investigated elements in only artificial extract of the 5 samples were performed by ICP-MS for control and comparison of the results found by TXRF. The results are given in Table 6. Cr, Co and Ni couldn't be measured exactly by ICP-MS in the extracts because of high background sourced from signals of other compounds of air and water, and also no information obtained about Hg by this technique.

In order to control the accuracy, the determination of metal ions in artificial sweat model solution containing analyte ions at levels given in OKO-TEX standard 100 were also performed by TXRF and ICP-MS. The results found by each techniques agree with each other (Table 7).

Table 6. Determination of some heavy toxic elements in artificial sweat extracts of 5 textile samples with ICP-MS for controlling and comparison with others techniques

	Element (mg/ Kg textile)								
Sample	Cr	Co	Ni	Cu	Zn	As	Cd	Sb	Pb
Sweat Bl.	*	0.0002	0.004	0.014	0.034	*	0.004	0.0003	0.002
Sweat+ St.	*	0.019	0.165	1.206	1.672	0.015	0.009	0.017	0.034
D	*	0.007	0.012	0.027	0.090	0.003	0.009	0.017	0.034
E	*	0.003	0.010	0.046	4.022	0.005	0.001	0.007	0.038
G	*	0.005	0.016	0.008	0.103	0.003	0.001	0.006	0.001
T	*	0.003	0.015	0.018	0.168	0.005	*	0.011	0.008
Z	*	0.006	0.009	0.023	0.247	0.005	0.001	0.001	0.002

*: Below the detection limit

Table 7.The standard values of some heavy toxic elements in artificial sweat and obtained results by ICP-MS and TXRF techniques.

Concentration (mg/L)			
	in model solution	Found by ICP-MS	Found by TXRF
Cr	0.10	*	0.08
Co	0.20	0.186	0.16
Ni	0.20	0.165	0.17
Cu	1.25	1.21	1.11
Zn	2.50	1.67	1.95
As	0.01	0.015	0.015
Cd	0.01	0.009	*
Sb	-	0.017	*
Pb	0.04	0.034	0.032
Hg	0.01	*	*

Only tree elements mercury, cadmium and arsenic were determined in 4 textile samples by AAS in Textilinstitut at Krefeld. The results are given in Table 8.

Table 8. Determination of some heavy elements in 4 extract of textile by
Atomic Absorption Spectrometry.

	Element (mg/ Kg textile)		
Sample	As	Cd	Hg
D	< 0.08	0.073	< 0.08
N	< 0.08	0.023	< 0.08
R	< 0.08	0.040	< 0.08
T	< 0.08	0.045	< 0.08

CONCLUSION

TXRF technique is suitable for the simultaneous determination of 8 trace elements in the textile samples. It can be concluded that TXRF is not suitable for Hg and Cd. Because, determination of Cd and Hg in trace amount have some problems with TXRF technique and their limit levels in the textile samples are below the detection limit of TXRF. It was possible to reach to the limit value for Hg by the cold vapor technique. Also cadmium must be determined by TS-FF-AAS or GFAAS

Any metal ion could be find except Ni, Cu, Zn with a higher concentration than the limit values of ÖKO-TEX 100 in any textile sample. The concentration of Ni, Cu and Zn in 3 different samples of 25 textiles were higher then the values of the ÖKO-TEX-100. These samples are generally cotton flannel and has the worst quality. On the other hand, the amount of Pb in sweat extracts are higher than the textile’s in some samples, therefore the results are not suitable for the conclusion for Pb.

The results found by TXRF are comparable with the results found by ICP-MS. ICP-MS gives not more information than TXRF, especially for the elements with the lower elements.The element contents of textile samples are different from each other as ‘finger print type, TXRF-spectrum. This technique can also be used for the identification of textile sample in criminal investigation.

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