

Introduction to Elemental Analysis by ED-XRF

Justin Masone Product Specialist 3 June 2015

Shimadzu Corporation



- Established in 1875. Headquartered in Kyoto, Japan
- Ranked Top 5 Instrument Providers in the world by Chemical and Engineering News
- Offer broad range of analytical solutions and technologies



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- •
- •

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X-ray

- XRD
- XRF
- EDX •

Balances & Scales



DSC









What is XRF?

- Analytical method to determine the <u>elemental</u> composition of many types of materials
- Can be used to determine the thickness and composition of layers, coatings, and platings.
- Fast, accurate, non-destructive
- Requires minimal sample prep



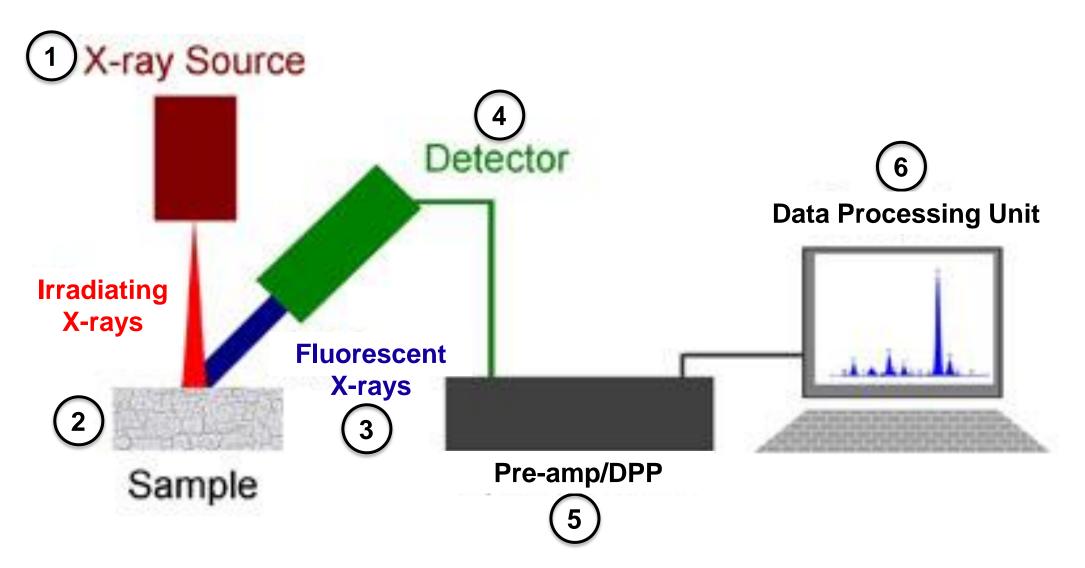
Samples can be in solid, liquid, powder, or filtered form

What is ED-XRF?

Energy-Dispersive X-Ray Fluorescence

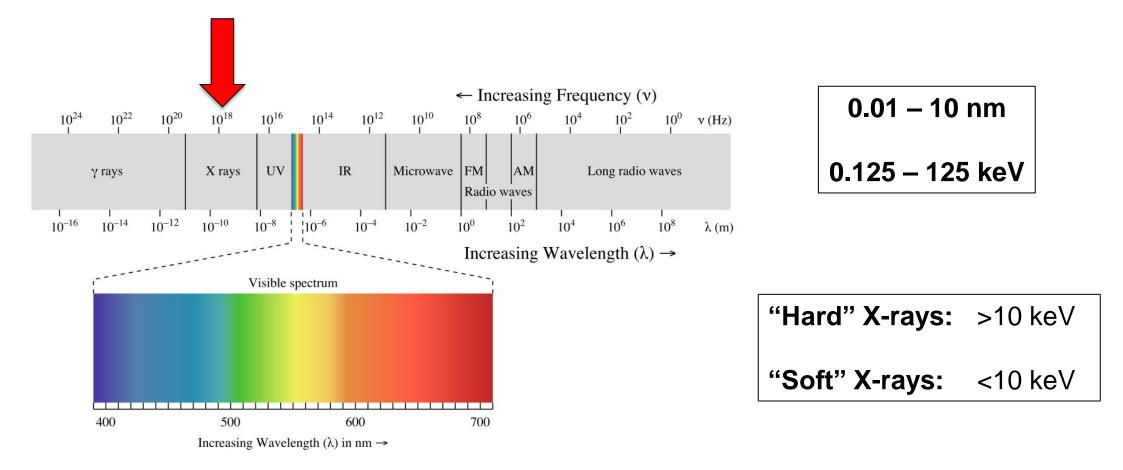
- **Energy-dispersive**: Ability to discern the energies of x-rays
- <u>X-Ray</u>: Form of energy; source of ionizing radiation
- **Fluorescence**: Phenomenon of absorbing energy (short λ) and subsequently emitting energy (longer λ)

Basis of EDX



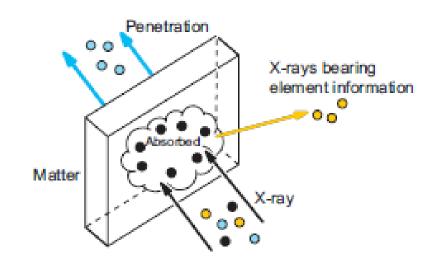
What are X-Rays?

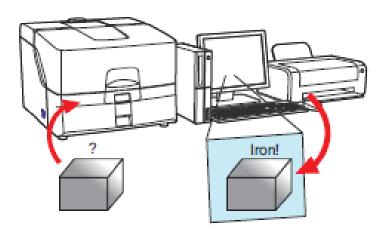
• X-rays are a kind of electromagnetic energy:



How Do X-Rays Interact with Matter?

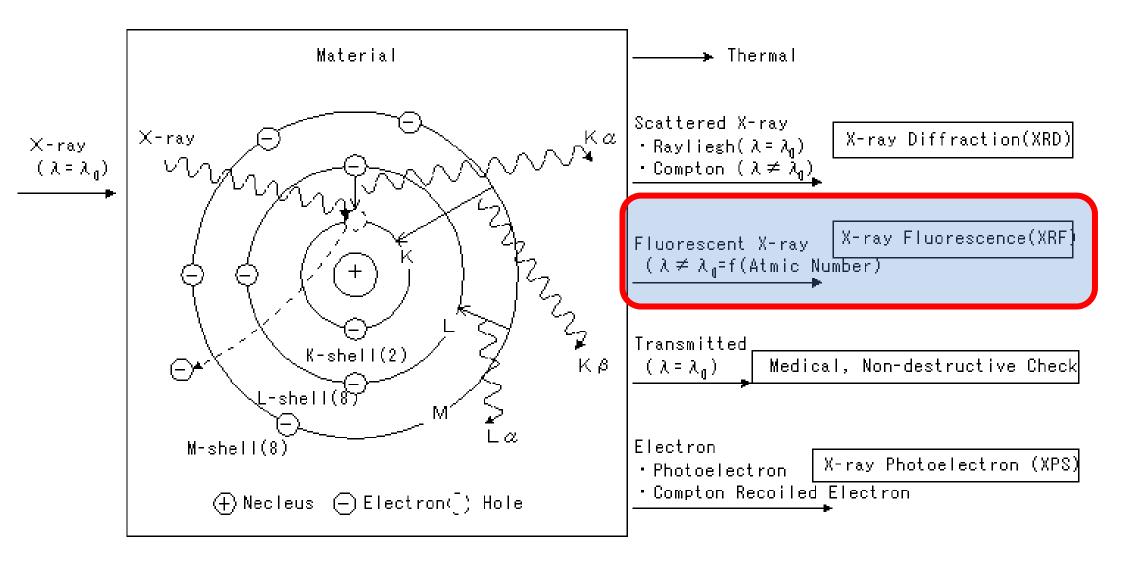
- When X-rays strike matter, some of them are absorbed and some pass through
- Absorption and penetration depend on the elemental composition, density, and thickness of matter.
- A consequence of absorption is that <u>secondary X-rays are</u> <u>generated</u>, which are characteristic of that matter:



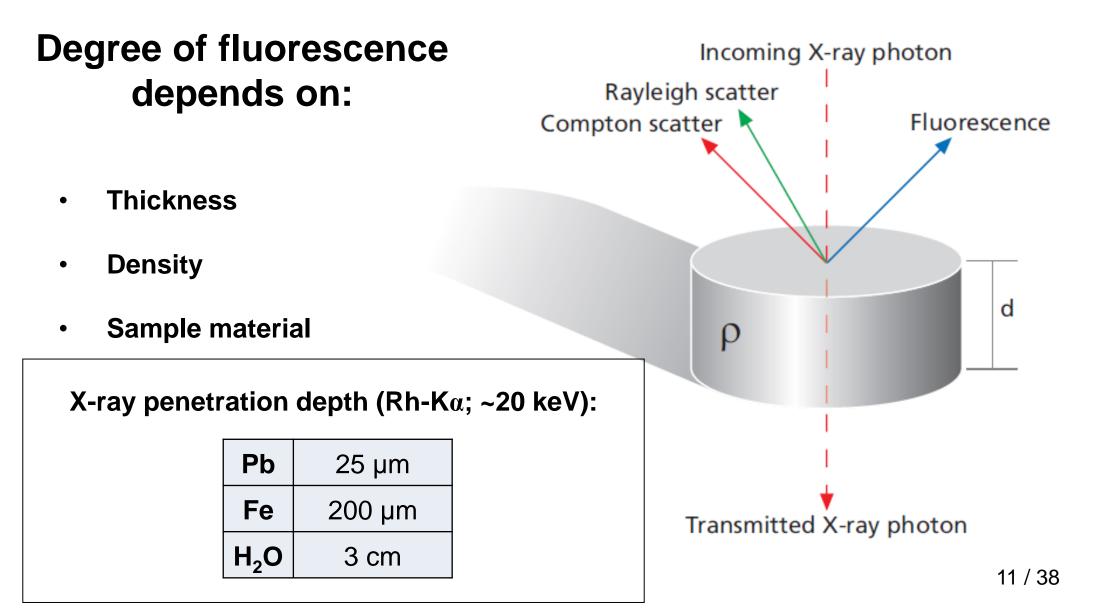


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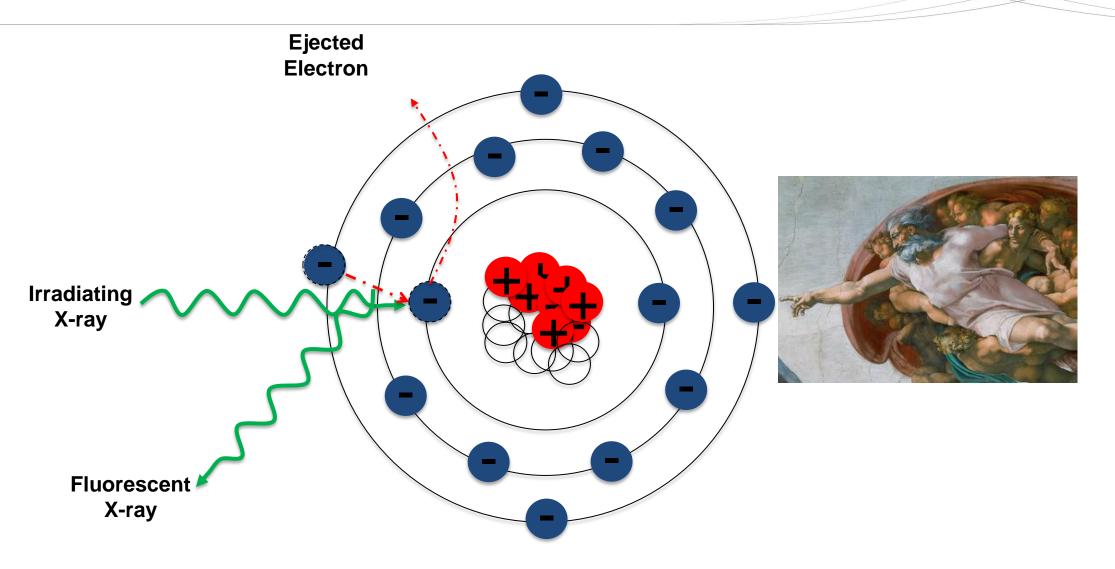
How Do X-Rays Interact with Matter?



How Do X-Rays Interact with Matter?

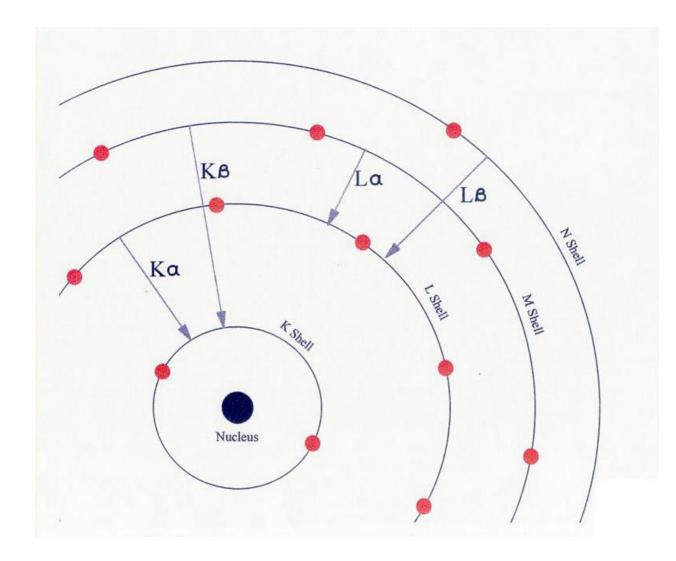


How Do X-Rays Interact with Atoms?



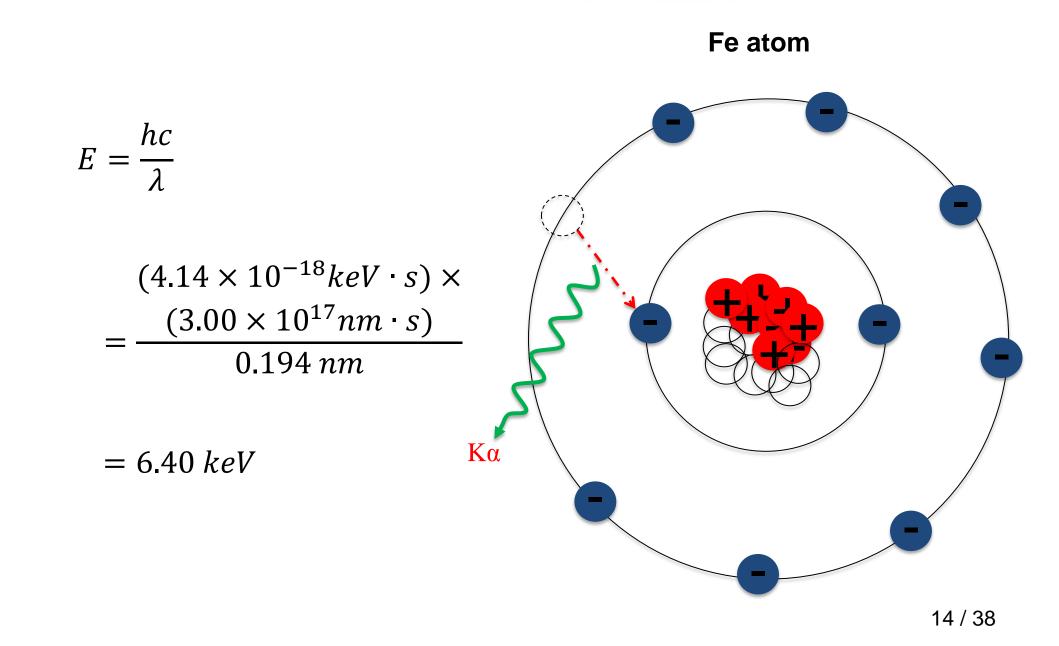
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Types of Transitions



These are "Characteristic X-rays"

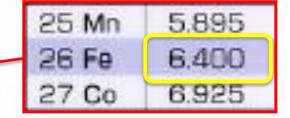
Energy of X-Rays: Example



Energy of X-Rays: Example

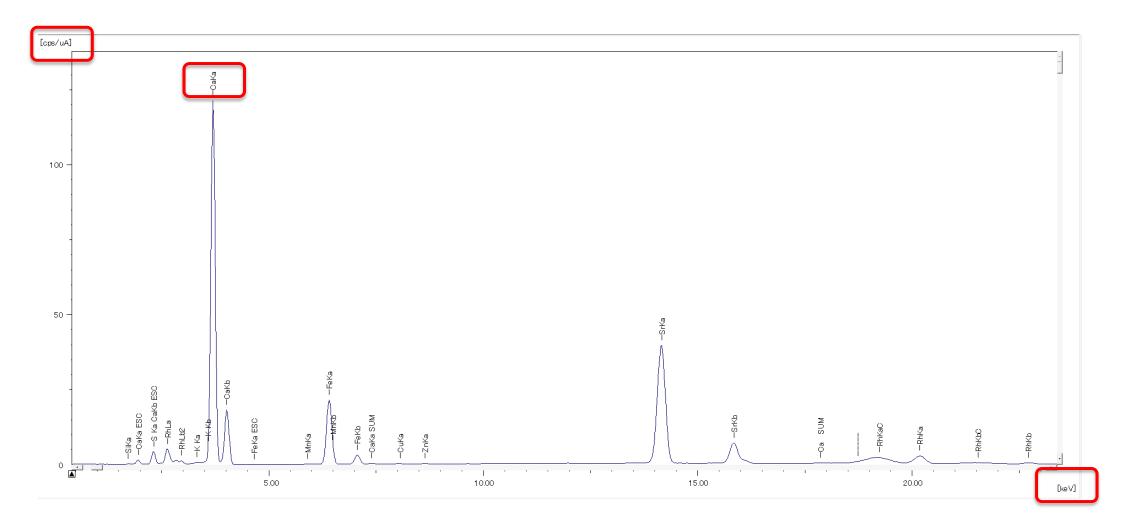
Energy Table

elemen	t Kα	KB1	Kab	La1	L <i>B</i> 1	LB2		Llab	Lilab	Lillab	Mal
55 Cs	30.857	34.985	35.990	4.287	4.620	4.936	5.281	5.721	5.358	5.012	
56 Ba	32.071	36.381	37.458	4.466	4.828	5.157	5.531	5.996	5.623	5.247	
57 La	33.302		38.940	4.651	5.042	5.384	5.789	6.268	5.889	5.484	0.83
58 Ce	34.575	39.261	40.452	4.840	5.262	5.613	6.052	6.548	6.161	5.724	0.88
59 Pr	35.865			5.034	5.489	5.850	6.322	6.835	6.439	5.963	0.92
60 Nd	37.188	42.272	43.580	5.231	5.722	6.090	6.602	7.130	6.724	6.210	0.97
61 Pm	n 38.541	43.826	45.201	5.433	5.962	6.339	6.892	7.436	7.014	6.461	
62 Sm	n 39.918	45.416	46.858	5.636	6.205	6.587	7.178	7.748	7.314	6.718	1.08
63 Eu	41.328	47.035	48.526	5.846	6.457	6.843	7.481	8.061	7.620	6.981	1.13
64 Gd	42.768	48.698	50.237	6.058	6.714	7.103	7.786	8.386	7.932	7.243	1.18
65 Tb	44.233	50.380	52.007	6.273	6.978	7.367	8.102	8.717	8.253	7.516	1.24
66 Dy	45.734	52.116	53.790	6.495	7.248	7.636	8.419	9.055	8.583	7.790	1.29
67 Ho	47.268	53.883	55.624	6.720	7.526	7.912	8.747	9.400	8.917	8.068	1.34
68 Er	48.813	55.674	57.480	6.949	7.811	8.189	9.089	9.758	9.262	8.358	1.40
69 Tm	50.421	57.507	59.380	7.180	8.102	8.469	9.426	10.121	9.617	8.650	1.40
70 Yb	52.051	59.380	61.318	7.416	8.402	8.759	9.780	10.491	0.070	8.944	1.52
71 Lu	53.696	61.288	63.290	7.656	8.709	9.049	10144	10.874	10.345	9.249	1.58
72 Hf	55.400	63.225	65.324	7.899	DOLL	9.348	10.516	11.274	10.737	9.558	1.64
73 Ta	57.110	65,221	CT. IEU	8.146	9,343	9.652	10.896	11.682	11.133	9.877	1.71
74 W	50.072	67.237	69.498	8.398	9.673	9.962	11.286	12.100	11.539	10.200	1.77
75 Re	60.658	69.304	71.668	8.653	10.010	10.276	11.686	12.531	11.955	10.531	1.84
76 Os	62.492	71.420	73.845	8.912	10.355	10.599	12.096	12.972	12.381	10.868	1.91
77 Ir	64.341			9.175	10.709	10.921	12.512	13,424	12.820	11,212	1.98
78 Pt	66.267	75.739	78.372	9.443	11.071	11.251	12.942	13.883	13.273	11.563	2.05
79 Au	68.199	77.978	80.719	9.714	11.443	11.585	13.382	14.353	13,736	11.922	2.12
80 Hg	70.167	80.249	83.100	9.989	11.823	11.924	13.830	14.843	14.215	12.287	2.19
81 TI	72.168		85.507	10.269	12.214	12.272	14.292	15.343	14.701	12.661	2.27
82 Pb			87.995	10.552	12.614	12.623	14.765	15.855	15.205	13.041	2.34
83 Bi	76.345			10.839	13.024	12.980	15.248	16,376	15.720	13.427	2.42
84 Po	78.472	89.779	a contractor	11.131	13.447	13.340					
85 At				11.427	13.876		16.252				
86 Rn				11.728	14.315		16.771				-
87 Fr	85.096			12.032	14.771	14.450					-
88 Ra		100.14	4	12.341	15.235	14.841	17.850				
89 Ac		102.80	7	12.653	15,714	14.041	18,409				-
90 Th			109.624		16.203	15.625		20,463	19.683	16.299	2.99
91 Pa				13.292	16.703	16.025	19.568	21,172	20.362	16.768	3.08
92 U		111.29		The second states a second	17.220	16.428	20.167		20.947		3.17
93 No		113.748		13.945		16.841	20.785			17.100	0.17
94 Pu		110.74		10.040	17.700	10.041	20.700				
95 An		- 22						-			
96 Cm											
97 Bk											-
98 Cf											
99 Es											
100 Fm					-			-			-
100 Pil											
102 No											-
102 No											
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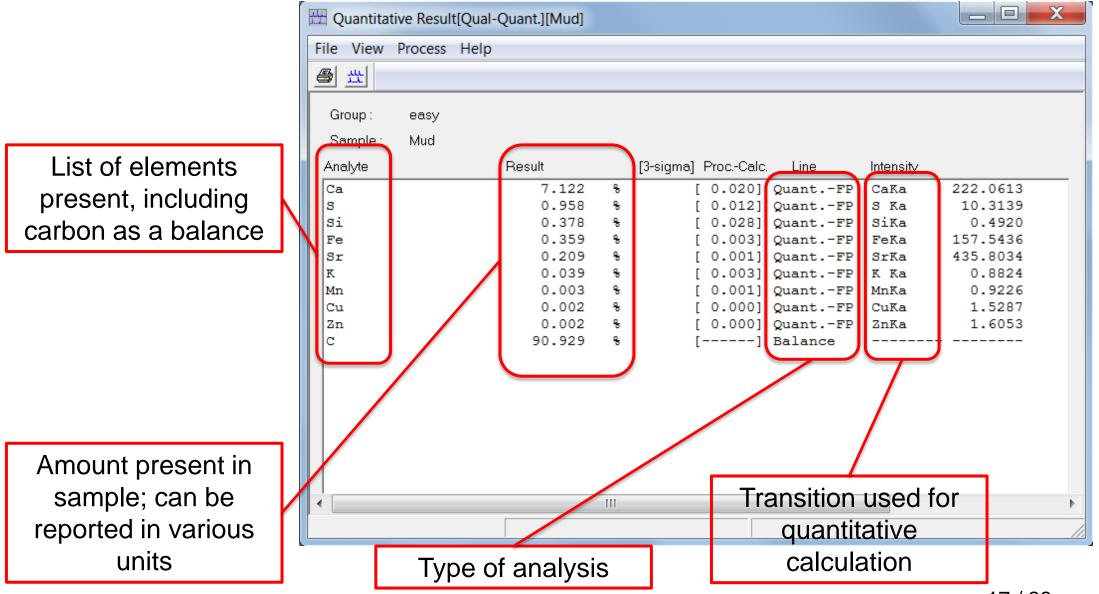




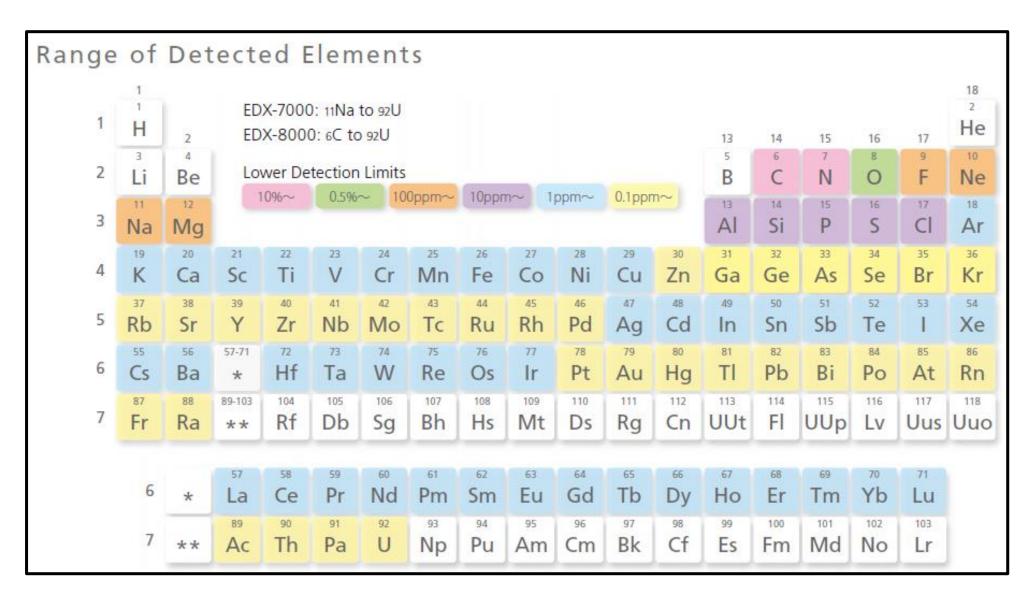
EDX Spectrum



EDX Data Output

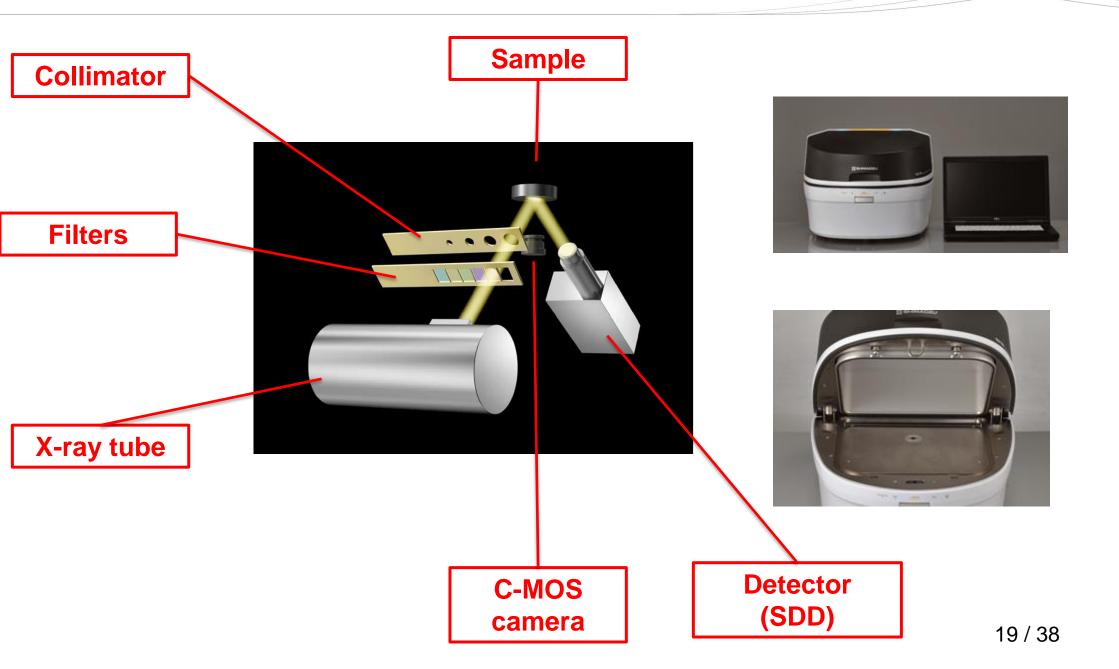


Analytical Range



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EDX System



Why use EDX?

- Elemental analysis is traditionally done by AA/ICP
 - This requires significant sample prep and cost of analysis is high
 - With EDX, there is:
 - Minimal to no sample prep (solvents, TDS, etc. are not a concern)
 - Detection limits for heavy (high Z) elements ≤ 0.1 ppm
 - Low cost of analysis in terms of both time and money
 - No gas requirements
 - No exhaust
 - No sample waste
 - Uses less bench space
 - Easy to use

Example Applications

Electrical/electronic materials

- RoHS and halogen screening
- Thin-film analysis for semiconductors, discs, liquid crystals, and solar cells

Automobiles and machinery

- ELV hazardous element screening
- Composition analysis, plating thickness measurement, and chemical conversion coating film weight measurement for machine parts

Ferrous/non-ferrous metals

- Main component analysis and impurity analysis of raw materials, alloys, solder, and precious metals
- Composition analysis of slag

Mining

Grade analysis for mineral processing

Ceramics

Analysis of ceramics, cement, glass, bricks, and clay

Oil and petrochemicals Analysis of sulfur in oil

- Analysis of additive elements and mixed elements in lubricating oil

Chemicals

- Analysis of products and organic/inorganic raw materials
- Analysis of catalysts, pigments, paints, rubber, and plastics

Environment

Analysis of soil, effluent, combustion ash, filters, and fine particulate matter

Pharmaceuticals

- Analysis of residual catalyst during synthesis
- Analysis of impurities and foreign matter in active pharmaceutical ingredients

Agriculture and foods

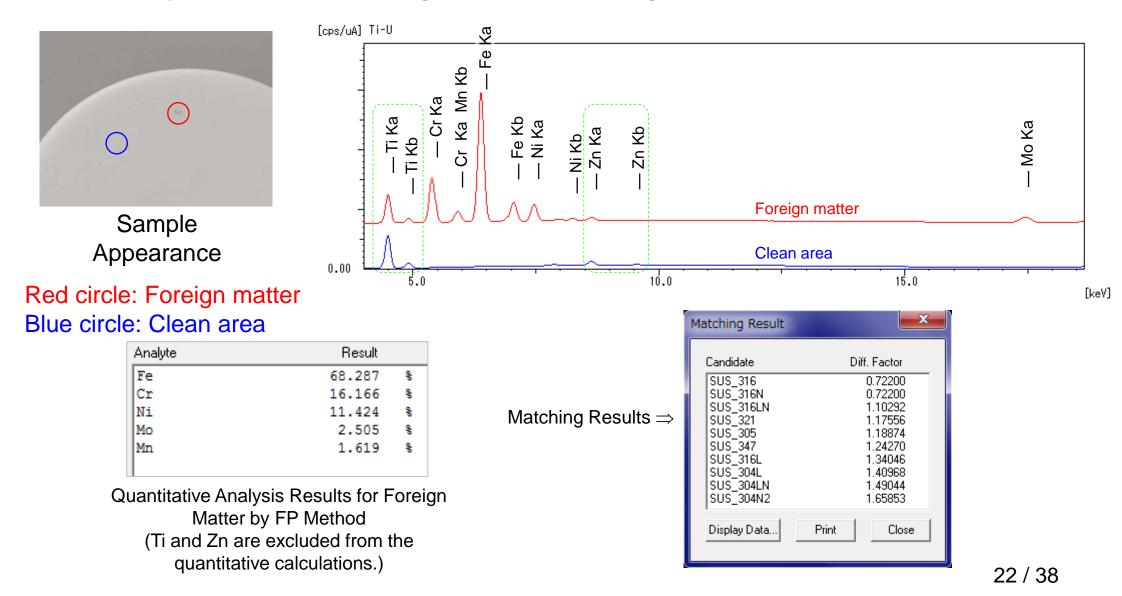
- Analysis of soil, fertilizer, and plants
- Analysis of raw ingredients, control of added elements, and analysis of foreign matter in foods

Others

Composition analysis of archeological samples and precious stones, analysis of toxic heavy metals in toys and everyday goods 21/38

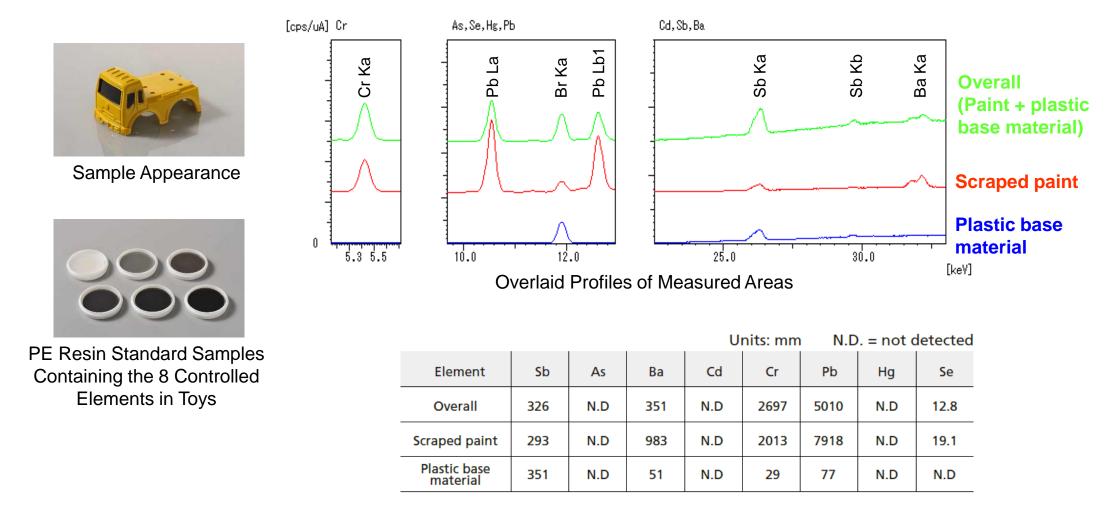
Application: Foreign Matter Identification

Analysis Example: Foreign Matter Adhering to a Plastic Extruded Part



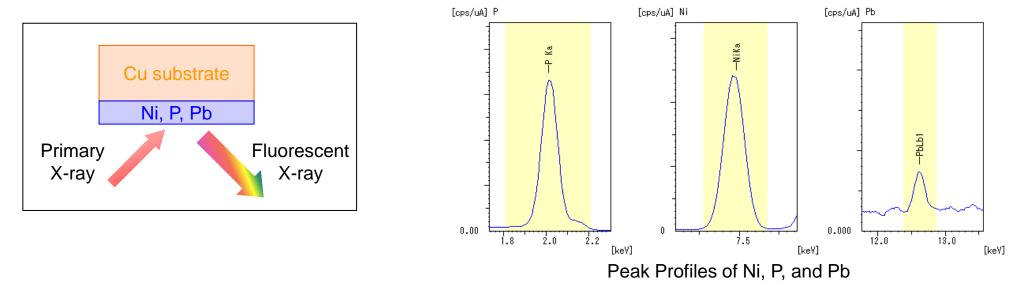
SHIMADZU Application: Hazardous Substances in Products

Analysis Example: Screening Analysis for 8 Controlled Elements in Toys



Application: Thin Films

Analysis Example: Film Thickness and Composition Measurements of Electro-less Nickel Plating



Laye	r Info	Analyte	Result		[3-sigma]	ProcCalc.	Line
1	Layer1						
1	Layer	Layer1	1.805	um	[]	Total	
1	Elem.	P	11.244	8	[0.036]	QuantFP	P Ka
1	Elem.	Ni	88.738	8	[0.145]	QuantFP	NiKa
1	Elem.	Pb	0.018	8	[0.003]	QuantFP	PbLb1
в	Base						
в	Elem.	Cu	100.000	÷.	[]	Fix	

Quantitative Analysis Results by Film FP Method

Application: Cement

Analysis Example: Qualitative Analysis of Cement

Sample

NIST Certificate of Analysis Standard Reference Materials® Portland Cement SRM 1880b, 1881a, 1884b, 1886a, 1887b, 1888b, 1889a Table 1 shows the standard values.

							l	[11d5570]
	SiO2	AI_2O_3	Fe ₂ O ₃	CaO	MgO	SO₃	K₂O	Na _z O
1880b	20.42	5.183	3.681	64.16	1.176	2.710	0.646	0.091
1881a	22.26	7.060	3.090	57.58	2.981	3.366	1.228	0.199
1884b	19.30	4.851	2.937	61.31	4.740	4.034	0.957	0.278
1886a	22.38	3.875	0.152	67.87	1.932	2.086	0.093	0.021
1887b	19.59	4.911	2.471	61.15	3.624	4.599	0.961	0.288
1888b	20.42	4.277	3.062	63.13	3.562	2.634	0.658	0.136
1889a	20.66	3.89	1.937	65.34	0.814	2.690	0.605	0.195

Table 1 Standard Values

[mass%]

Application: Cement

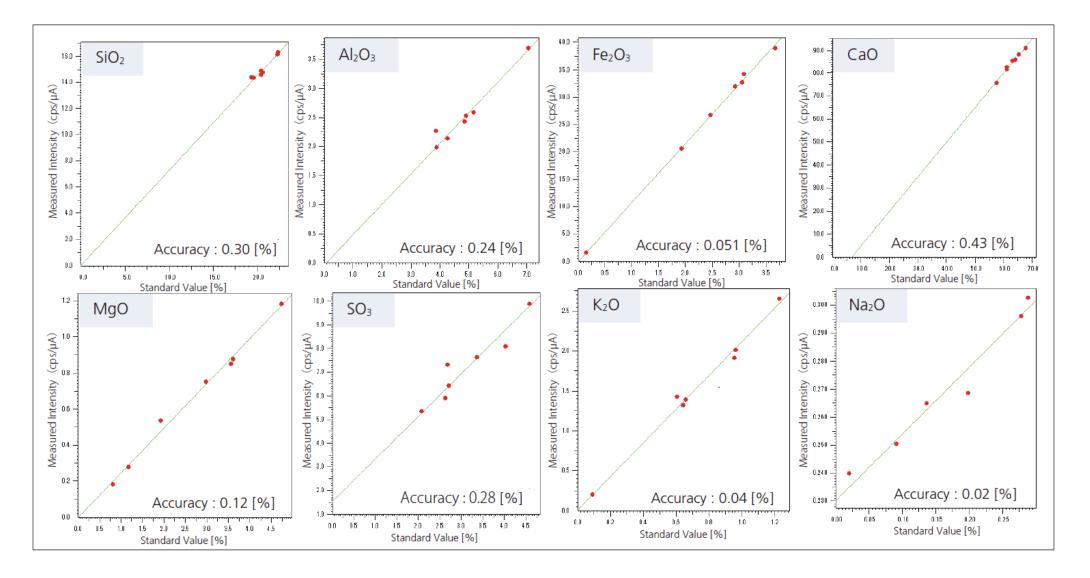
Sample Preparation

Pressure forming was conducted using a vinyl chloride ring (inner diameter 35 mm ϕ), with a total pressure of 250 kN for 60 seconds. A photograph of the sample is shown in Fig. 1.



Fig. 1 Pressure-Formed Briquette of Cement

Application: Cement



Application: Cement

Lower Limits of Detection (L.L.D.)

The lower limits of detection calculated using the above calibration curves are shown in Table 2.

Table 2 Lower Limits of Detection (300 sec, 100 sec only for Fe ₂ O ₃)								[mass%]
	SiOz	Al _z O ₃	Fe ₂ O ₃	CaO	MgO	SO₃	K _z O	NazO
Lower Limit of Detection (LLD)	-	0.0083	0.0022	-	0.0157	0.0066	0.0049	0.0159

Repeatability

Using the above calibration curve method, the repeatability test results for SRM 1880b shown in Table 3 were obtained by simply conducting 10 repeat

measurements. The X-ray fluorescence spectra for each measurement element of each sample are shown in Fig. 3.

Table 3 Repeatability for SRM 1880b (300 sec, 100 sec only for Fe ₂ O ₃)								[mass%]
	SiOz	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO3	K2O	Na ₂ O
1	20.09	5.032	3.615	64.12	1.088	2.729	0.622	0.100
2	20.05	5.031	3.609	64.15	1.087	2.740	0.621	0.098
3	20.04	5.043	3.615	64.18	1.087	2.736	0.612	0.107
4	20.01	5.022	3.625	64.16	1.089	2.738	0.616	0.105
5	19.96	5.038	3.618	64.18	1.148	2.744	0.620	0.100
6	20.02	5.045	3.625	64.18	1.094	2.744	0.615	0.114
7	20.11	5.052	3.630	64.18	1.157	2.743	0.616	0.110
8	20.09	5.037	3.628	64.17	1.174	2.740	0.619	0.112
9	19.98	5.032	3.631	64.17	1.101	2.741	0.616	0.109
10	20.14	5.040	3.614	64.21	1.158	2.745	0.621	0.100
Average	20.05	5.037	3.621	64.17	1.118	2.740	0.618	0.105
Standard Deviation	0.059	0.008	0.008	0.025	0.036	0.005	0.003	0.006
Coefficient of Variation [%]	0.30	0.17	0.22	0.04	3.2	0.17	0.52	5.5

Application: Polymer Film

Analysis Example: Determination of Thickness and Concentration



 Shimadzu's newly-developed "Background FP" method (BG-FP) incorporates X-ray scattering theory into the standard FP calculation

 Uses Compton scattering to determine thickness of a polymer film while simultaneously determining its constituent elements

Scattered Radiation

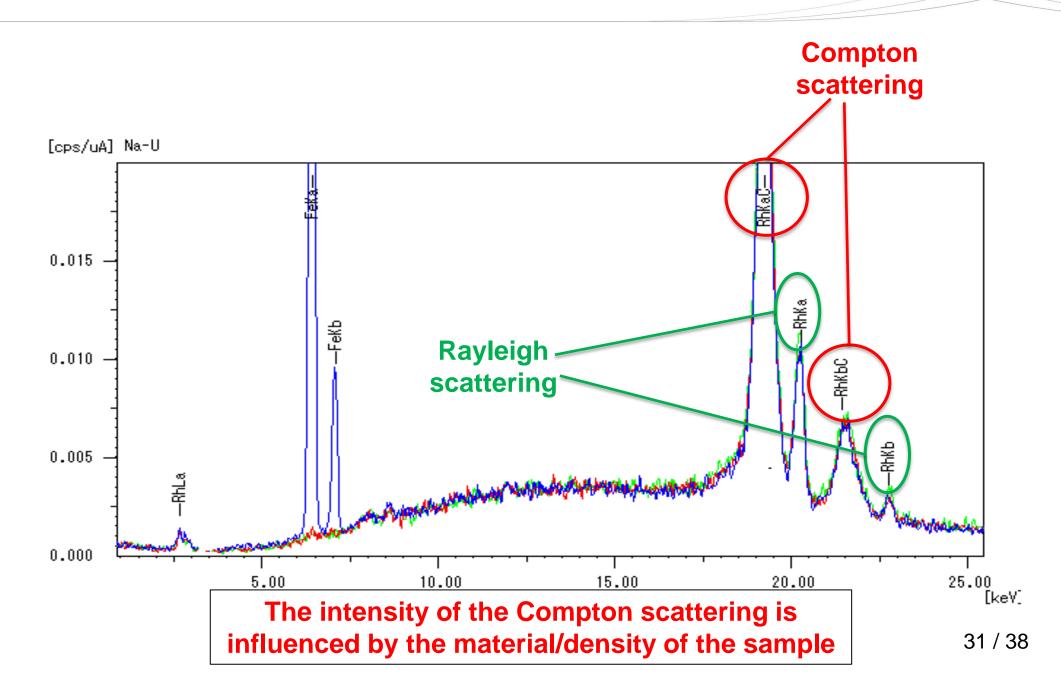
Some of the X-rays from the tube do not generate fluorescent X-rays when they strike the sample. Instead, they are scattered within the sample. There are two types scattering radiation:

Compton Scattering: When the source characteristic X-rays (Rh) that strike the material suffer from some energy loss (inelastic scattering)

Rayleigh Scattering: When the source characteristic X-rays (Rh) strike the sample without any change in energy (elastic scattering)

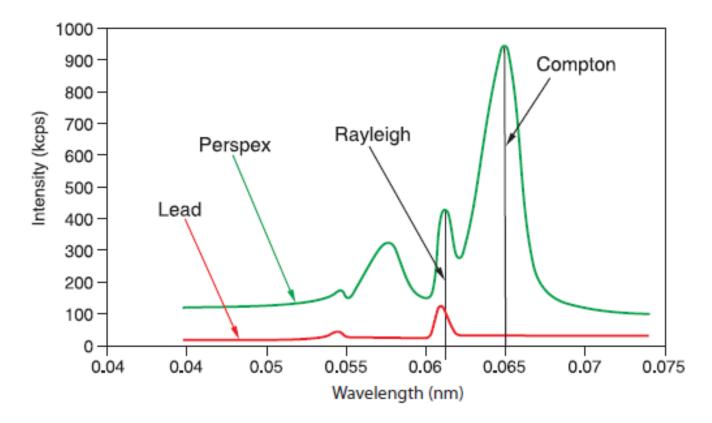
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Application: Polymer Film



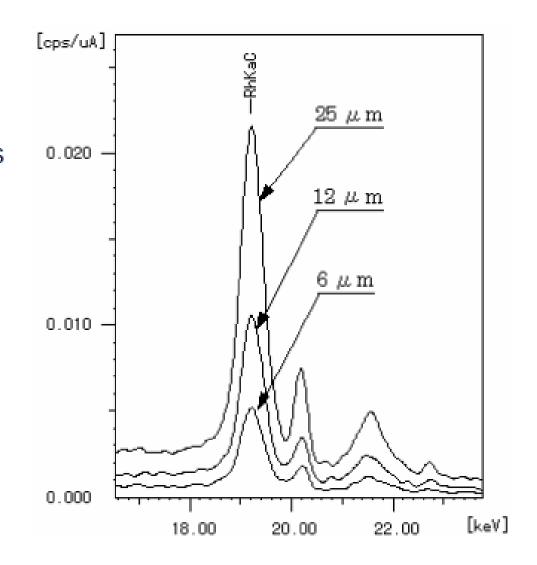
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- Samples with light elements give rise to high Compton scatter and low Rayleigh scatter
 - This is because they have more loosely bound electrons
- With very heavy elements, the Compton scattering disappears completely



Application: Polymer Film

Qualitative Analysis of Polyester Films In the BG-FP method of polymer film thickness determination, the Compton scattering lines of the "characteristic" X-rays of the X-ray tube target (Rh) is measured. The RhKa Compton scattering profiles of the 3 polymer films of differing thickness is shown superimposed on the same graph in Fig. 2. From this it can be seen that the intensity of the RhKa Compton scattering lines becomes greater as the thickness of the film increases.



Determining the Thickness of Polyester Films The results of the thickness determination analysis by BG-FP method are shown in Table 1. In order to calculate the film's thickness the density of the film is required. In this case the 1.39 g/cm3 density of polyester is used. In addition it was assumed that the composition of the film was $C_{10}H_8O_4$.

Table 1	Thickness D	etermination	of Polvest	ter Films by	/ Background FF	^o Method
_	-		2			

Sample	Chemical Formula	Film Density	Determined Value	Reference Value	by Micrometer
Polvester	(C ₈ H ₁₀ O ₄)n	1.39 a/cm ³	7.2 μm 14.5 μm	6 μm 12 μm	7-14 µm 14 um
Films	(0811004)	1.55 g/cm	29.7 µm	25 µm	26-30 µm

Determination of Both the Thickness and the Concentration

The thickness of polyethylene that includes the elements Cr, Mn, Fe, Co, Ni, Cu and Zn was determined at the same time as the content of the elements within the polyethylene. The quantitative profiles are shown in Fig. 3, while in Table 2 the values calculated from the quantitative profiles by the BG-FP method is shown together with their equivalent area density (30 mm_{ϕ}) conversion values and standard values. Note that the major was assumed to be polyethylene (CH₂)n and used as the balance(residue balance), while the density of the film was assumed to be that of polyethylene (0.92 g/cm³).

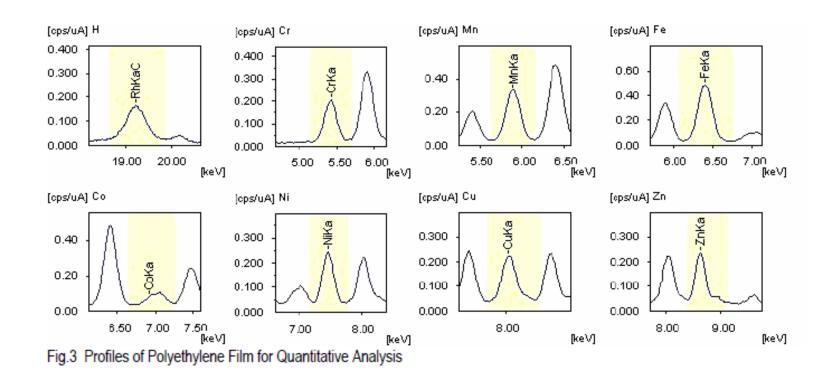


Table 2 Determined Thickness and Concentration of/in Polyethylene Film by Background FP Method

Sample	Film Density	Determined	Standard Value		
Polyethylene Film including Inorganic Compounds	0.92 g/cm ³ ((CH ₂)n)	Cr 91 µg/30 mmφ Mn 297 Fe 219 Co 21 Ni 87 Cu 85	(645 ppm) (2096) (1546) (149) (612) (598)	100 μg/30mmφ (300 200 20 100 100	769ppm) (2307) (1538) (154) (769) (769)
		Zn 88 Thickness 218 µm	(620)	100 200 µm	(769)

Application Notes

Screening Analysis with EDX-7000 Navi Software

Quantitative Analysis of Elements in Small Quantity of Organic Matter by EDXRF

- New Feature of Background FP Method -

Quantitative Analysis of Cement by EDX-8000

Quantitative Analysis of Waste Oil by EDX-7000

TC Measurement and Elemental Composition Analysis of Fly Ash

- Quantitation by TOC and XRF -

Quantitative Analysis of Tin (Sn) in Plastics by EDXRF

Analysis of Aqueous Solution by EDX-LE

- Performance in Air Atmosphere -

Quantitative Analysis of Fluorine (₉F) by EDXRF

Quantitative Analysis of Antimony (Sb) in Plastics by EDXRF

Qualitative and Quantitative Analysis of Seafood by EDXRF

EDXRF Analysis of Arsenic and Lead in Dietary Supplement

QC Analysis of Magnesium Alloy Die Castings by EDXRF

EDXRF Analysis of PM2.5 (Particle Matter)

EDXRF Analysis of Sulfur and Other Elements in Oil

EDXRF Analysis of Lead, Cadmium, Silver, Copper in Lead-Free Solder Materials

Determination of Arsenic and Lead in Earth and Sand Using EDXRF [JIS K 0470]

Comparison of Calibration Curves of Lead, Cadmium and Chromium in Zinc Alloy and Copper Alloy

EDXRF Analysis of Lead, Cadmium, Mercury and Chromium in Zinc Alloy

EDXRF Analysis of Chlorine in Irregularly Shaped Plastic Samples

Analysis of Foreign Matter in Food Using EDX

EDXRF Analysis of Heavy Elements in a Toy and a Cup

EDXRF Analysis of Chlorine in Plastic (PE) Materials

Analysis of Sulfur in Oil Using Energy Dispersive X-Ray Fluorescence Spectrometer

Analysis of Foreign Matter Using CCD

EDXRF Analysis of Arsenic in Foods

Additional Information

Additional Information:

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