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Application News

No.X250

X-ray Analysis

Analysis of Aqueous Solution by EDX-LE – Performance in Air Atmosphere –

The EDX-LE is an instrument that facilitates analysis, management and output for restriction of hazardous substances (RoHS) screening, used in the identification of heavy metals such as cadmium, lead, chromium and mercury (Cd, Pb, Cr, Hg), halogens like bromine and chlorine (Br, Cl), as well as other potentially hazardous elements, such as antimony (Sb). Handling of these analyses has become simplified, as they can now be conducted in an air atmosphere without the need for liquid nitrogen. This opens up the applicability of such analyses to include quality management and acceptance as well as pre-shipment inspection in the manufacturing process. As an example of some of these performance features, we present the measurement results of an aqueous standard solution of 18 elements, Al–Pb, under air atmospheric conditions, as well as their respective calculated lower limits of detection and repeatability.

Elements and Samples

(1) 1000 ppm standard solution
Silicon, Potassium, Calcium, Chromium, Zinc, Arsenic, Selenium, Ruthenium, Rhodium, Antimony, Barium, Samarium, Lead (Si, K, Ca, Cr, Zn, As, Se, Ru, Rh, Sb, Ba, Sm, Pb)
(2) 100 ppm standard solution
Nickel, Zinc (Ni, Zn)
(3) Multi-element mixed standard solution
Phosphorus (P) 1000 ppm
(4) Prepared solution
Aluminum (Al): 50,000 ppm, Chlorine (Cl): 971 ppm

Preparation

Approximately 5 mL of each of sample were transferred to a container over which 5 µm thick polypropylene film was then stretched.

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

The theoretical lower limits of detection were calculated from the measurement element spectral intensity (NET, BG) using the following expression.

$$L.L.D. = 3 \cdot \frac{C}{NET} \cdot \sqrt{\frac{BG}{A \cdot T}}$$

Intensity: [*cps*/µA], *C*: concentration in aqueous solution [*ppm*]
A: Current value [µA], *T*: Integration time [sec]

Fig. 1(a) and (b) show the expected lower limits of detection of the unmeasured elements predicted using the interpolation calculation based on the measured elements. Here, the integration time is 100 sec.

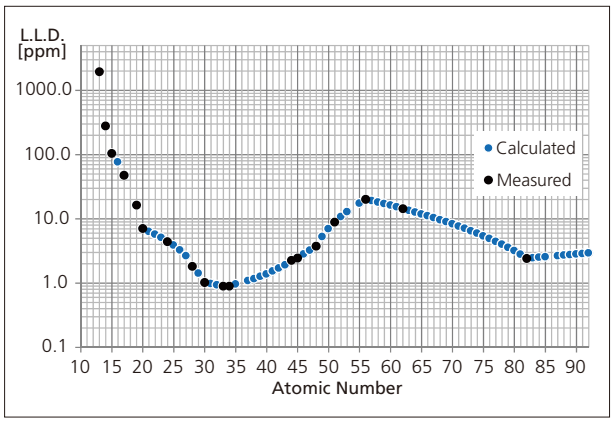

Fig. 1 (a) L.L.D. to Atomic Number

Fig. 1 (b) L.L.D. [ppm] on Periodic Table

Na	Mg											Al **1950**	Si **278**	P **104**	S 77	Cl **48**	Ar –
K **17**	Ca **7.1**	Sc 6.4	Ti 5.8	V 5.2	Cr **4.4**	Mn 3.9	Fe 3.3	Co 2.7	Ni **1.9**	Cu 1.5	Zn **1.1**	Ga 1.0	Ge 1.0	As **0.9**	Se **0.9**	Br 1.0	Kr –
Rb 1.1	Sr 1.2	Y 1.3	Zr 1.4	Nb 1.6	Mo 1.8	Tc 2.0	Ru **2.3**	Rh **2.5**	Pb 2.9	Ag 3.3	Cd **3.8**	In 5.3	Sn 7.0	Sb **9.0**	Te 11	I 13	Xe –
Cs 18	Ba **21**	*	Hf 7.1	Ta 6.6	W 6.0	Re 5.5	Os 5.0	Ir 4.5	Pt 4.0	Au 3.6	Hg 3.2	Tl 2.9	Pb **2.5**	Bi 2.5	Po 2.6	At 2.6	Rn –
Fr 2.7	Ra 2.8	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Uuu	Uub		Uuq		Uuh		

*	La 20	Ce 19	Pr 18	Nd 17	Pm 16	Sm **15**	Eu 14	Gd 13	Tb 12	Dy 12	Ho 11	Er 9.7	Tm 9.0	Yb 8.4	Lu 7.7
**	Ac 2.8	Th 2.9	Pa 2.9	U 3.0	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

* Lanthanide series, ** Actinide series

Measured, Calculated

Fig. 1 Lower Limit of Detection for Al-U in Aqueous Solution (100 sec)

Repeatability

We calculated the theoretical repeatability (1σ) from the spectral intensity (NET, BG) of the measured elements using the following expression. The results are shown in Table 1.

$$\sigma = \frac{C}{NET} \cdot \sqrt{\frac{NET+BG}{A \cdot T}}$$

Intensity: [*cps*/μA], *C*: concentration in aqueous solution [*ppm*]
A: Current value [μA], *T*: Integration time [sec]

X-Ray Fluorescence Spectrum

Fig. 2 shows the X-ray fluorescence spectra of the measured elements. Even light elements including silicon can be detected and analyzed in air atmosphere.

Conclusion

Detection and quantitative analysis of light elements in air atmosphere is generally considered to be difficult, but analysis is possible for silicon at a low concentration of a few hundred ppm to calcium at several ppm. Furthermore, heavy elements such as arsenic can be measured accurately at the 1 ppm level, with repeatability at 1 % or less.

Thus, performance similar to that seen with aqueous solutions can be obtained for additive elements in organic materials, such as resins (molds, powders) and films, etc. These techniques may also be applied to management analysis of particular elements, such as chromium, iron, copper and zinc in iron and non-ferrous metal smelting slag. The detector installed in the EDX-LE is a Si-PIN type semiconductor detector. Compared with the Si (Li) semiconductor type and Si-drift semiconductor type detectors, the overall analytical performance of the Si-PIN type is similar to these detectors, slight differences in spectral resolution notwithstanding.

Analytical Conditions

Instrument	: EDX-LE
Elements	: Al, Si, P, Cl, K, Ca, Cr, Ni, Zn, As, Se, Ru, Rh, Cd, Sb, Ba, Sm, Pb
Analytical Group	: Qual-Quan
X-ray Tube	: Rh target
Tube Voltage [kV]	: 15 (Al-Cr, Ba, Sm), 50 (Ni-Sb, Pb)
Current [μA]	: Auto
Primary Filter	: without (Al, Si, P), #1 (Ru, Rh, Cd, Sb), #2 (Cl, K, Ca, Cr, Ba, Sm), #4 (Ni, Zn, As, Se, Pb)
Collimator [mmϕ]	: 10
Atmosphere	: Air
Detector	: Si-PIN
Integration Time [sec]	: 100
Dead Time [%]	: Max 40 %

Note 1) As performance will vary depending on the material (principal component) and coexisting elements, it is not the same.
Note 2) Please utilize the optional function add-on kit.

Table 1 Theoretical Precision of Repeatability

Element	Al	Si	P	Cl	K	Ca	Cr	Ni	Zn
Concentration [ppm]	50,000	1,000	1,000	971	1,000	1,000	1,000	100	100
Standard Deviation [ppm]	891	97.9	38.3	21.7	8.79	5.13	2.58	1.21	0.85
Coefficient of Variation [%]	1.8	9.8	3.8	2.2	0.88	0.51	0.26	1.2	0.85

Element	As	Se	Ru	Rh	Cd	Sb	Ba	Sm	Pb
Concentration [ppm]	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000
Standard Deviation [ppm]	1.78	1.68	2.86	3.87	4.00	5.56	8.85	6.04	2.46
Coefficient of Variation [%]	0.18	0.17	0.29	0.39	0.40	0.56	0.89	0.60	0.25

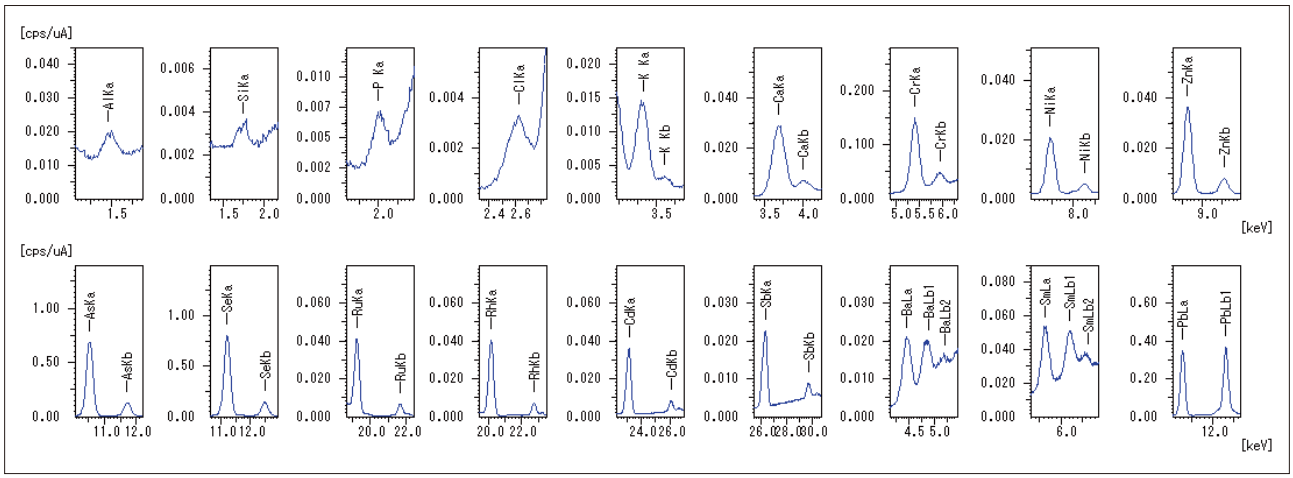

Fig. 2 X-Ray Fluorescence Spectra of Measured Elements

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