ANALYSES OF TRACE ELEMENTS IN WATER SOLUTION USING HIGH SENSITIVITY INSTILLATION PAPER FILTER

1. INTRODUCTION

The influence of trace heavy elements dissolved in water, such as Cd, Pb, As, Cr and Se, on the environment is widely noticed as a big social problem. To prevent this problem, water quality must always be analyzed and monitored. By reason of the number of samples for water quality analyses, an analysis sequence must be as simple, rapid and reproducible as possible.

Although there are many analysis methods for trace elements such as the ICP spectrometry and atomic absorption analysis, from the viewpoint of the above-mentioned simplicity, rapidness and reproducibility the X-ray fluorescence analysis is one of the excellent analysis methods. It is also known that the X-ray fluorescence analysis has advantages in that it can analyze elements from B to U simultaneously and does not contaminate the inside of an instrument thanks to its non-contact and non-destructive features.

We have improved the instillation method, which is the simplest sample pretreatment method that has been generally used for the X-ray fluorescence analysis to measure trace elements in water solution, and developed a new method that can analyze them at a tens of ppb level. Details are described below:

2. ANALYSIS PERFORMANCE OF HIGH SENSITIVITY INSTILLATION METHOD

An outline of a high sensitivity instillation paper filter (ultracarry) is as follows: It is a very simple object; a very thin film on which special paper is stuck to collect elements. To reduce scattered rays that worsen limits of detection, the paper has been made thinner than those of conventional instillation paper filters. The new filter also has an advantage in that 500µL of solution can be instilled at a time, compared to 50µL in the case of conventional filters.

Limits of detection achievable using this application for elements

Table 1 List of Limits of Detection Unit: ppb

Element	Limit of Detection	Element	Limit of Detection
B	30ppm	Zn	18
F	1ppm	As	16
Na	76	Se	24
P	56	Sr	25
K	12	Mo	27
V	34	Ag	152
Cr	26	Cd	182
Mn	16	Sn	40
Fe	18	Sb	43
Co	17	Ba	105
Ni	20	Tl	81
Cu	19	Pb	76

Calculated for a measurement time of 100 sec. For measuring conditions, see “6. MEASURING CONDITIONS”.

are shown in Table 1. Limits of detection at a tens of ppb level have been obtained for the elements. The values are better than those of the conventional instillation paper filter method by one order of magnitude or more.

3. MEASUREMENT RESULT (EXAMPLE OF SCREENING ANALYSIS USING SQX)

To check the performance of the high sensitivity instillation paper filter method, an SQX (Scan Quant X) analysis (semiquantitative analysis) was made using the standard sample LPC Standard1 (containing 20 ppm of each element) manufactured by SPEX.

The SQX analysis is a method to analyze thin film samples and bulk samples using the FP (fundamental parameter) method. It makes semiquantitative calculations using the X-ray intensities of elements identified from a whole angle qualitative spectrum without using standard samples. In an unknown measurement, we do not know elements contained in a sample at all in many cases. It is one of the important steps for reducing analysis errors to measure a whole angle qualitative spectrum and take account of the influence of coexisting elements and spectrum lines adjacent to that of an analyzed element. “More accurate semiquantitative analysis through a whole angle qualitative spectrum” - this is our traditional concept of the semiquantitative analysis.

Furthermore, the SQX has a new “fixed angle measurement mode” and carries out fixed time counting at a peak angle and background angles to reduce statistical errors resulting from a counting time.

An analysis result is shown in Table 2. Although Pb-Lα, Zn-Lβ1 and Mo-LL overlap with As-Kα, Na-Kα and P-Kα respectively as interfering lines, a correction calculation is made automatically by the theoretical overlap correction incorporated in the SQX. Although the values are a semiquantitative analysis result obtained using the FP method, they show very good correlation.

Table 2 Semiquantitative Analysis Result Using SQX

Unit: ppm

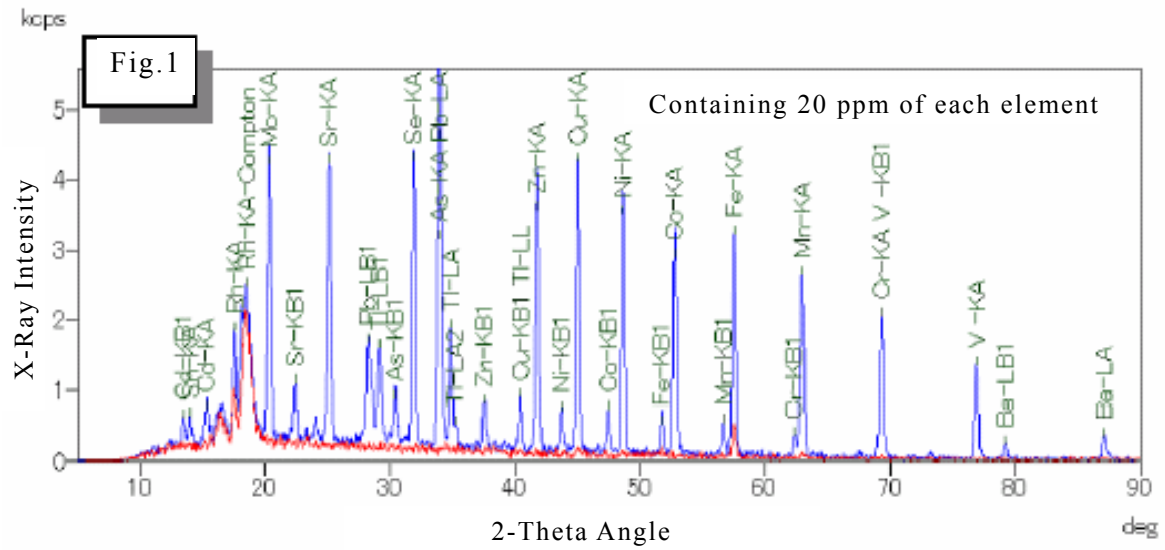
Element	SQX Analysis Value	Standard Value	Element	SQX Analysis Value	Standard Value
Na	18	20	As	21	20
P	72	100	Se	19	20
K	92	100	Sr	20	20
V	18	20	Mo	19	20
Cr	20	20	Ag	3	5
Mn	21	20	Cd	20	20
Fe	20	20	Sn	18	20
Co	20	20	Sb	22	20
Ni	21	20	Ba	18	20
Cu	19	20	Tl	20	20
Zn	19	20	Pb	18	20

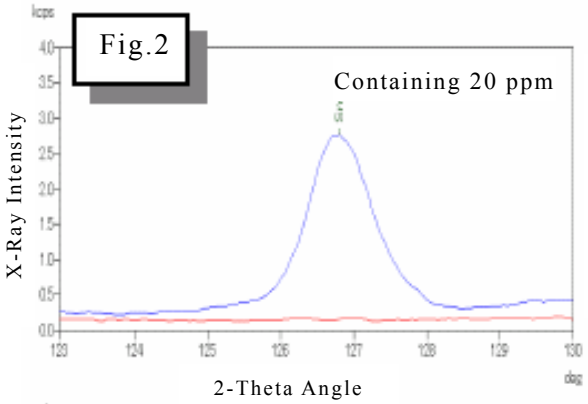
4. QUALITATIVE SPECTRA

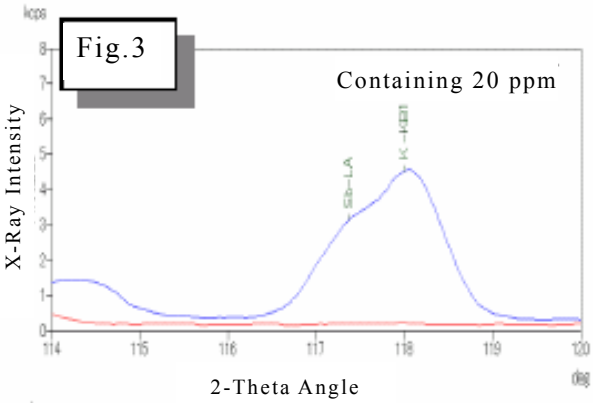
The qualitative analysis spectra of the elements measured in the SQX analysis are shown below:

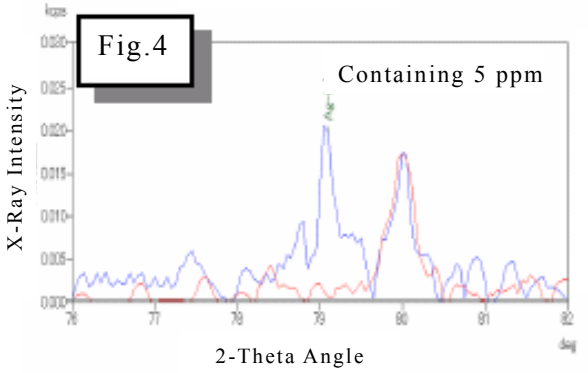
Fig.1: Ti-U, Fig.2: Sn-Lα, Fig.3: Sb-Lα (K-Kβ1 overlaps.), Fig.4: Ag-Lα,
Fig.5: Cd-Lα (Rh-Lγ1 overlaps.), Fig.6: P-Kα (Mo-LL overlaps.),
Fig.7: Na-Kα (Zn-Lβ1 overlaps. The peak on the high angle side is Zn-Lα.)

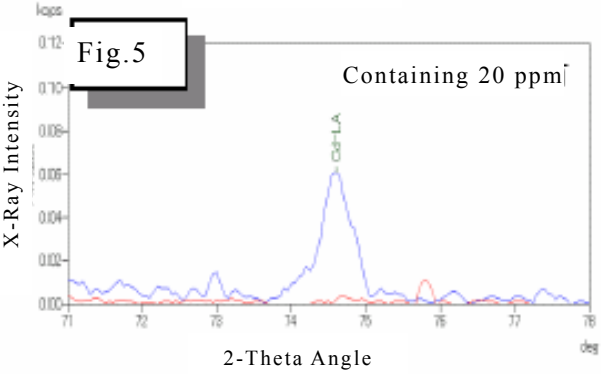
The qualitative analysis spectra of the elements have been obtained very clearly.

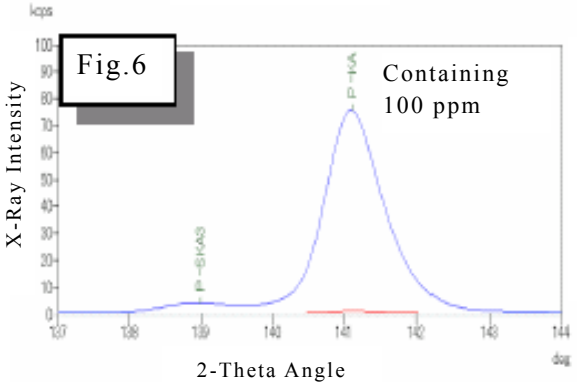


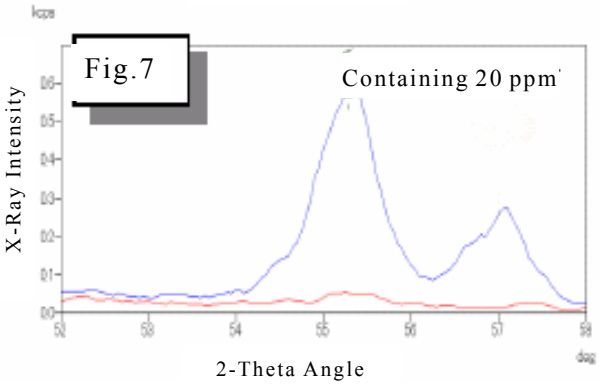












5. SAMPLE PREPARATION

After 500µL of standard solution SPEX LPC Standard1 was instilled on a high sensitivity instillation paper filter (ultracarry), the filter was dried.

6. MEASURING CONDITIONS (SQX ANALYSIS CONDITIONS)

Instrument : ZSX Primus Series
X-Ray Tube : Rh target end window type
Measurement Diameter : 30mm

Measured Element	Ti-U	Ca	K	Cl	S
kV-mA	50-48	40-60	40-60	30-80	30-80
Primary X-Ray Filter	-	-	-	-	-
Slit	S2	S4	S4	S2	S4
Analyzing Crystal	LiF(200)	LiF(200)	LiF(200)	Ge	Ge
Detector	SC	F-PC	F-PC	F-PC	F-PC

Measured Element	P	Si	Al	Mg	Na
kV-mA	30-80	30-80	30-80	30-80	30-80
Primary X-Ray Filter	-	-	-	-	-
Slit	S4	S4	S4	S4	S4
Analyzing Crystal	Ge	PET	PET	RX25	RX25
Detector	F-PC	F-PC	F-PC	F-PC	F-PC

Measured Element	F	Sn	Sb	Ag	Cd
kV-mA	30-80	40-60	40-60	30-80	30-80
Primary X-Ray Filter	-	-	-	Al	Al
Slit	S4	S4	S4	S2	S2
Analyzing Crystal	RX25	LiF(200)	LiF(200)	Ge	Ge
Detector	F-PC	F-PC	F-PC	F-PC	F-PC

A fixed angle measurement was made for each element.

7. CONCLUSION

We have explained that trace elements in water solution can be analyzed easily at a tens of ppb level using the high sensitivity instillation paper filter (ultracarry).

Since measurements can be made with very simple sample preparation, it is expected that personal errors in analyses can be substantially reduced.

This is a non-destructive and non-contact analysis method in which a measured sample is irradiated with primary X-rays (excitation rays). It therefore does not cause the contamination of the instrument at all.

Since this method produce no waste liquid in sample preparation, it is an environment-friendly analysis method.

If solution is condensed beforehand, analyses at a 10 ppb level will be possible for checking against water quality standards and effluent standards.

Although the description has been given for the ZSX Primus series, this method can also be used for ordinary scan type X-ray fluorescence spectrometers.

Ultracarry:

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