APPLICATION REPORT

Rigaku

Trace element analysis for water solution via high-sensitivity micro-droplet method

1. Introduction

Influence of trace heavy elements in water such as Cd, Pb, As, Cr, Se, etc. on the environment is treated as serious social problem. In order to control this problem, water quality must be monitored. Considering the high number of test samples required for assessment of water quality, the examination necessitates a simple, rapid, and reproducible analysis method.

With respect to simplicity, speed, and reproducibility, X-ray fluorescence (XRF) analysis is a superior analysis method. There are many other analysis methods for trace elements, such as ICP-OES and AA, but XRF analysis has the advantages of analyzing B-U in a single analysis sequence and that the measurement can be done without contamination inside a spectrometer. XRF is non-destructive, non-contact technique of analysis.

For trace element analysis of liquid samples with an XRF spectrometer, a micro-droplet method has been generally used. An improved micro-droplet method which enables the analysis of several 10ths of a ppm has been developed. In this report, this new method is shown.

2. Performance of the high-sensitivity micro-droplet method

High-sensitivity filter paper (Ultra Carry) has a simple structure. A specially developed paper for capturing elements is place on a very thin film. Compared to normal filter paper for a micro-droplet method, thinner paper is used here in order to reduce scattering, which degrades the lower limit of detection (LLD). Moreover, 500µL can be dropped at a time, while only 50µL can be put on normal filter paper.

The LLDs with Ultra Carry were tabulated in Table 1. LLDs of several 10ths

Table 1.	The LLDs.	(Unit: p	pb)

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Element	LLD	Element	LLD
В	30ppm	Zn	18
F	1ppm	As	16
Na	76	Se	24
Р	56	Sr	25
K	12	Мо	27
V	34	Ag	152
Cr	26	Cd	182
Min	16	Sn	40
Fe	18	Sb	43
Co	17	Ba	105
Ni	20	TI	81
Cu	19	Pb	76

Measuring time: 100s; for details, refer to "6. Measuring condition".

of a ppm were obtained and are less than a tenth of the LLDs for a normal micro-droplet method.

3. Analysis results (Screening analysis example by SQX)

For testing the performance of Ultra Carry, an SQX (Scan Quant X) analysis was performed on the standard solution SPEX LPC Standard 1.

SQX is standardless quantification program for bulk or thin-film sample using a Fundamental Parameter (FP) method. It calculates concentrations using the intensities of detected elements found through a qualitative analysis. Since there are many times when it is not clear what elements are contained in 'unknown' samples, it is necessary to reducing analytical errors that every element is detected in the qualitative spectra and that the influences of co-existing elements and spectra close to the element lines of analytes are considered. "Qualitative spectra lead to better results of semi-quantitative analysis": this is the traditional position of RIGAKU for semi-quantitative analysis. In addition, SQX has a "fixed-angle measurement" function. Intensities are counted in fixed time at 20 angles of both a peak and background which reduces statistical errors related to measuring time.

The SQX results are shown in Table 2. For semi-quantitative analysis, superior results were obtained. Though As-K α , Na-K α , and P-K α are overlapped by Pb-L α , Zn-L β 1, and Mo-LL respectively, the results for these elements were also good. SQX has a theoretical overlapping correction function which automatically operates during the quantitative calculation.

Element	SQX result	Std. value	Element	SQX result	Std. value
Na	18	20	As	21	20
Р	72	100	Se	19	20
K	92	100	Sr	20	20
V	18	20	Мо	19	20
Cr	20	20	Ag	3	5
Mn	21	20	Cd	20	20
Fe	20	20	Sn	18	20
Со	20	20	Sb	22	20
Ni	21	20	Ba	18	20
Cu	19	20	TI	20	20
Zn	19	20	Pb	18	20

Table 2. The semi-quantitative analysis (SQX) results. Unit: ppm

4. Qualitative scan spectra

The qualitative spectrum of each element obtained in the SQX analysis was shown as follows:

Fig. 1. Ti-U. Fig. 2. Sn-L α . Fig. 3. Sb-L α (overlapped by K-K β 1).

Fig. 4. Ag-L α . Fig. 5. Cd-L α (overlapped by Rh-L γ 1 derived from the tube).

Fig. 6. P-K α (overlapped by Mo-LL).

Fig. 7. Na-K α (overlapped by Zn-L β 1; the peak at a higher angle is Zn-L α).

A clear spectrum of each element was obtained for trace elements.





5. Sample preparation

 $500 \mu L$ of the standard solution SPEX LPC Standard 1 was dropped on Ultra Carry, and it was dried.

6. Measuring condition (SQX analysis)

Spectrometer	: ZSX100e
X-ray tube	: Rh target, End window

Measuring area $\,:\,$ 25mm $\!\phi$

Element	Ti - U	Ca	K	CI	S
kV-mA	50-48	40-60	40-60	30-80	30-80
Primary filter	-	-	-	-	-
Slit	Standard	Standard	Standard	Fine	Standard
Crystal	LiF(200)	LiF(200)	LiF(200)	Ge	Ge
Detector	SC	F-PC	F-PC	F-PC	F-PC
Element	Р	Si	AI	Mg	Na
kV-mA	30-80	30-80	30-80	30-80	30-80
Primary filter	-	-	-	-	-
Slit	Standard	Standard	Standard	Standard	Standard
Crystal	Ge	PET	PET	TAP	TAP
Detector	F-PC	F-PC	F-PC	F-PC	F-PC
Element	F	Sn (Lα)	Sb (Lα)	Ag (Lα)	Cd (Lα)
kV-mA	30-80	40-60	40-60	30-80	30-80
Primary filter	-	-	-	AI	AI
Slit	Standard	Standard	Standard	Fine	Fine
Crystal	TAP	LiF(200)	LiF(200)	Ge	Ge
Detector	F-PC	F-PC	F-PC	F-PC	F-PC

Fixed angle measurement was done for each element.

7. Conclusion

The high-sensitivity filter paper (Ultra Carry) enables an analysis of several 10ths of a ppm of trace elements in water solution. Since sample preparation is simple and easy, it is possible to reduce analytical errors derived from sample handling. XRF, where primary X-rays are radiated onto samples, is a non-destructive and non-contact measurement; therefore, there is no contamination to the spectrometer. With respect to the environment, XRF is clean analysis because no waste solution occurs in sample preparation for analysis.

When the sample solution is concentrated, it is possible to apply Ultra Carry to obtain 10 ppb levels in analysis of river and waste water standards.

Ultra Carry can be used for other models than ZSX series.



*** Ultra Carry***

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