Trace Elemental Analysis of Commercial Bottled Drinking Water by a Portable Total Reflection X-ray Fluorescence Spectrometer

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A portable total reflection X-ray fluorescence spectrometer was applied to commercial bottled drinking water containing 62 ppb ($\mu\text{g/L}$) V, 7.5 ppm (mg/L) Ca, and 1 ppm K. A dry residue, prepared by repeated pipetting and drying a 20 μL portion of drinking water on a sample holder six times, and another dry residue, prepared by pipetting and drying a 120 μL portion of the drinking water, were measured. The size of the dry residue of the drinking water was reduced by repeating the pipetting and drying. Calcium and potassium were easily detected in these two dry residues. Vanadium was detected in the dry residue prepared by repeated pipetting and drying. Vanadium, calcium, and potassium were quantified by using an internal standard, and the average quantified concentrations of V, Ca, and K were 91 ppb, 8.2 ppm, and 1.5 ppm, respectively. Although these quantified concentrations deviated from the certified concentrations (62 ppb of V, 7.5 ppm of Ca, and 1 ppm of K), it was possible for this portable spectrometer to estimate approximate concentrations.

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The total reflection X-ray fluorescence (TXRF) analysis,^{1,2} which was first proposed by Yoneda and Horiuchi,³ was used for environmental analysis as follows. TXRF analysis was applied to rain water,⁴ atmospheric aerosols in a city,⁵ river water,⁶ soils,⁷ seawater,⁸ and biofilms.⁹ It has been possible for TXRF analysis to perform simultaneous multi-elemental determinations, measurements in air, and measurements of microliters of samples. Using a high-power X-ray source has reduced the detection limit for elements. Wobrauschek *et al.*¹⁰ reported that using a monochromatized synchrotron radiation for TXRF analysis achieved femtogram detection limit. TXRF spectrometers with a high-power X-ray tube, such as a rotating anode X-ray tube, have also detected low amounts of elements. These TXRF spectrometers have been stationary because the high-power X-ray tube has required water (several L/min) for cooling an anode, and have been operated with a few kW to a few tens of kW of power. In contrast to high-power X-ray tubes, air-cooled low-power X-ray tubes have not required cooling water, and have been operated with a few watts to tens of watts of power. These spectrometers have enabled to perform on-site analysis. Waldschläger¹¹ reported on a portable TXRF spectrometer with a 40 W X-ray tube, and its application to environmental samples. Mages *et al.*¹² reported that on-site analysis of environmental samples was performed by a portable TXRF spectrometer, which evolved from the spectrometer reported by Waldschläger.¹¹ Yamada *et al.*¹³ reported on a portable TXRF spectrometer with a 50 W X-ray tube, and its application to near-surface analysis of flat glasses manufactured by float glass process. Kunimura and Kawai¹⁴ have designed, constructed and reported a portable TXRF spectrometer with a 1.5 W X-ray tube. This portable spectrometer consisted of the low-power X-ray tube, a waveguide-type slit, and a Si PIN photodiode detector. These components were contained in a

housing made from Pb-containing acrylic slabs (equivalent to a 0.3 mm thick Pb plate). The size of this housing was 23 cm in height, 30 cm in width, and 9 cm in depth. This portable spectrometer was 5 kg, but most of this weight was due to the housing. Although the continuum X-rays emitted from the low-power X-ray tube were used for the excitation of fluorescent X-rays, 1 ng detection limit for Cr was achieved. This portable spectrometer was applied to leaching test solution of soils, and ppm concentrations or nanograms of S and Ca were detected.¹⁵ In the present report, this portable spectrometer was applied to commercial bottled drinking water containing 62 ppb of vanadium.

Experimental

Instrument

Details of this portable spectrometer were reported in a previous paper,¹⁴ and are briefly summarized here. An X-ray tube, "N6601" (Hamamatsu Photonics Co., Hamamatsu, Japan), was used in the portable spectrometer. It was operated at 9.5 kV and 150 μA . The X-ray tube with a transmission-type anode material, tungsten, emitted continuum X-rays because the maximum X-ray energy emitted from the X-ray tube was 9.5 keV, whereas the W L_1 , L_2 , and L_3 absorption edge energies were 12.1, 11.5, 10.2 keV, which were more than 9.5 keV X-ray energy. A waveguide-type slit, which consisted of two parallel Si wafers, was placed between the X-ray tube and a specimen in order to obtain a parallel X-ray beam; the waveguide-type slit restricted the X-rays to be 50 μm in height and 10 mm in width. Sánchez¹⁶ presented an X-ray focusing tool for TXRF analysis which also consisted of two parallel Si wafers, "plate beam-guides". Ayala¹⁷ proposed a TXRF spectrometer with a planar X-ray waveguide. A quartz optical flat (30 mm in diameter, and 10 mm in thickness) was used as a sample holder. Fluorescent X-rays were excited by the parallel X-ray beam illuminating a

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specimen on the optical flat. Although X-ray fluorescence (XRF) spectra, which were reported in previous papers,^{14,15} were measured by a Si PIN photodiode detector, "X-123", (Amptek Inc., Bedford, MA) containing a preamplifier and a digital signal processor in the detector housing, XRF spectra were measured by a Si PIN photodiode detector, "XR-100CR", containing a preamplifier in the detector housing (Amptek) in the present report. Effective detection area of these two detector was 7 mm². The signal from the detector was amplified by an amplifier, "PX2CR" (Amptek), and the amplified signal was taken into a personal computer through a multi-channel analyzer, "MCA8000A" (Amptek). The number of channels of the multi-channel analyzer was 512, and 1 channel corresponded to an X-ray energy of 27 eV. All measurements were performed in air at the glancing angle of 0.13° of the incident X-ray beam with respect to a quartz optical flat. The area where the surface of the optical flat was illuminated by the incident X-ray beams was about 20 mm in length, and 10 mm in width.

Sample preparation

Commercial bottled drinking water was measured. This bottle contained 500 mL of drinking water, and was made from polyethylene terephthalate (PET). The certified concentrations of V, Ca, and K were 62 ppb (µg/L), 7.5 ppm (mg/L), and 1 ppm, respectively. PET bottles for drinks are used only once, and are not recycled, in Japan. The sample was prepared by the following two methods:

1. A 20-µL portion of drinking water was pipetted onto the optical flat, and then it was dried on a heating plate. The pipetting and drying were repeated five times. The size of the dry residue was about 7 mm in diameter.
2. A 120-µL portion of the drinking water was pipetted onto the optical flat, and then dried on a heating plate. The size of the dry residue was about 17 mm in diameter.

These dry residues, which contained 7 ng of V, 900 ng of Ca, and 120 ng of K, were measured for 500 s.

Vanadium, calcium, and potassium in the drinking water were quantified by using an internal standard to compare the quantified concentrations with the certified concentrations, and Mn was used as the internal standard. A 20-µL portion of mixed standard solution containing 1 ppm of Ca, V, Cr, and Mn was measured in order to determine the relative sensitivities for the elements. The mixed standard solution was prepared from commercial 1000 ppm standard solution of Ca, V, Cr, and Mn. A 20-µL portion of the mixed standard solution was pipetted onto the optical flat, and was then dried on a heating plate. The mixed standard solution sample contained 20 ng of Ca, V, Cr, and Mn, respectively. Because the 1000 ppm Cr standard solution contained K₂Cr₂O₇, 0.75 ppm of potassium was contained in the mixed standard solution. Fifteen nanograms of K were also contained in the mixed standard solution sample. The size of the dry residue was about 2 mm in diameter, and the dry residue was measured for 1000 s. The relative sensitivities were determined by the following equation:

$$S_i = S_{\text{ref}} \left(\frac{C_{\text{ref}} I_i}{C_i I_{\text{ref}}} \right), \quad (1)$$

where S_i is the relative sensitivity for an elements, S_{ref} is the relative sensitivity for an internal standard element, I_i is the net intensity of fluorescent X-ray peaks of an element (counts/s), C_i is the concentration of an element (ppm), I_{ref} is the net intensity of fluorescent X-ray peaks of an internal standard element (counts/s), and C_{ref} is the concentration of an internal standard element (ppm). In the present paper, S_{ref} was defined as unity.

Fig. 1 Representative measured TXRF spectra of (a) a dry residue of drinking water of which size is about 17 mm in diameter, (b) a dry residue of the drinking water of which size is about 7 mm in diameter, and (c) the blank optical flat.

The drinking water and 10 ppm Mn standard solution were mixed in a 9:1 ratio. A 20-µL portion of the drinking water containing 1 ppm of Mn as an internal standard was pipetted onto the optical flat, and was then dried on a heating plate. The pipetting and drying were repeated six times. Three dry residues of drinking water containing 1 ppm of Mn were prepared, and their sizes were about 7 mm, 7 mm, and 10 mm in diameter, respectively. These three dry residues contained 140 ng of Mn, 8 ng of V, 945 ng of Ca, and 126 ng of K. These three dry residues were measured for 1000 s, and each dry residue was measured twice at two sample positions such that a region of a dry residue directly below the detector was changed. The areas of the three dry residues were larger than the effective detection area of the detector (7 mm²), and the detection sensitivities for elements in a region of a dry residue that was directly below the detector was the highest. The concentrations of V, Ca, and K in the mixed solution which were quantified by using an internal standard were also determined by Eq. (1). The S_i and S_{ref} values used for quantifying the elements were obtained from a measurement of the mixed standard solution containing 1 ppm of Ca, V, Cr, and Mn. The quantified concentrations of V, Ca, and K in the drinking water were 10/9 times as high as those determined by Eq. (1), because the drinking water was diluted by the Mn standard solution.

Fig. 2 Representative measured TXRF spectrum of a dry residue of mixed standard solution containing 1 ppm of Ca, V, Cr, and Mn, and 0.75 ppm of K.

Fig. 3 Representative TXRF spectra of a dry residue of drinking water containing 1 ppm of Mn as an internal standard element measured at different sample positions such that a region of the dry residue directly below the detector was changed.

Results and Discussion

Figure 1 shows representative measured TXRF spectra of (a, b) dry residues of drinking water and (c) the blank optical flat. Calcium and potassium were detected as shown in Figs. 1(a) and (b). Vanadium was not detected in Fig. 1(a). The area of the dry residue, of which size was about 17 mm in diameter, was larger than the area where the surface of the optical flat was illuminated by the incident X-ray beams, and the incident X-ray beams did not fully illuminate this dry residue. The area of the dry residue, of which size was about 7 mm in diameter, was smaller than the area illuminated by the incident X-ray beams. Consequently, the sensitivity of this portable spectrometer was increased by reducing the size of the dry residue, and vanadium was detected in Fig. 1(b). Sulfur and chlorine were also detected in Fig. 1(b). Argon was detected in all spectra in Fig. 1

Table 1 Representative results of the quantification of drinking water

	Concentration of an element, ppm		
	V	Ca	K
Dry residue 1a	0.044	7.7	1.3
Dry residue 1b	0.056	7.4	1.1
Dry residue 2a	0.100	14.2	2.2
Dry residue 2b	0.167	8.4	1.5
Dry residue 3a	0.111	6.3	1.3
Dry residue 3b	0.067	5.4	1.4
Mean value	0.091	8.2	1.5
Standard deviation	0.045	3.1	0.4

Three dry residues of drinking water (dry residues 1, 2, and 3) were measured; each dry residue was measured twice at different sample positions such that a region of the dry residue directly below the detector was changed.

as well as Si because the air contained 0.93 vol% Ar and the sample holder was SiO₂. The silicon K_α peak intensity in Fig. 1(b) was higher than that in Fig. 1(c). This result indicated that Si was also contained in this dry residue of the drinking water. The silicon K_α peak intensity in Fig. 1(b) was higher than that in Fig. 1(a). The spectral background in Fig. 1(b) was higher than that in Fig. 1(c). The increase of the background intensity resulted from scattered X-rays from the dry residue. The spectral background in Fig. 1(b) was higher than that in Fig. 1(a). The background intensity increased with an increase of the sample thickness; this result indicated that the thickness of the dry residue of which size was about 7 mm in diameter was more than that of the dry residue of which size was about 17 mm in diameter.

Figure 2 shows a representative measured TXRF spectrum of a dry residue of mixed standard solution. As shown in Fig. 2, K, Ca, V, Cr, and Mn were detected. Sulfur was detected because the 1000 ppm V standard solution contained 0.45 mol/L of H₂SO₄. The relative sensitivities for K, Ca, and V were 0.49, 1.35, and 1.16, respectively.

Figure 3 shows representative TXRF spectra of a dry residue of the drinking water containing 1 ppm of Mn as an internal standard element measured at different sample positions. As shown in Fig. 3, Mn, V, Ca, and K were detected, but the K and Mn K_α peak intensities in Fig. 3(a) were higher than those in Fig. 3(b). Table 1 gives representative results for the quantification of the drinking water. The average quantified concentrations of V, Ca, and K in the bottled drinking water were 91 ± 45 ppb (mean ± standard deviation), 8.2 ± 3.1 ppm, and 1.5 ± 0.4 ppm, respectively. The three dry residues were inhomogeneous because of repeating the pipetting and drying; it was possible that the distributions of K, Ca, V, and Mn were different. Consequently, the variability of quantified concentrations of these elements was happened as given in Table 1. However, it was possible for this portable spectrometer to estimate approximate concentrations.

Conclusions

A portable spectrometer with a 1.5 W X-ray tube was applied to commercial bottled drinking water containing 62 ppb of vanadium. Although the continuum X-rays emitted from the low-power X-ray tube were used as the excitation source, ppb concentrations or nanograms of vanadium were detected. In the

quantification of a sample, it was possible for this portable spectrometer to estimate the approximate concentrations of elements by a simple quantification. This kind of small and highly sensitive spectrometer is possible to be used for the rapid monitoring of elements in the field, or to be used for rapid sample screening before using large stationary elemental analyzers.

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