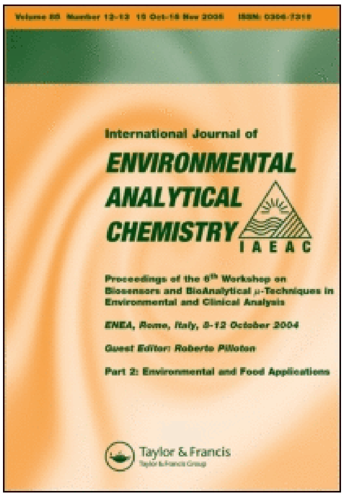

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Jingru, An and Qing, Zhang(1983) 'An Analytical Method of Ultra-Trace Tellurium for Samples of Sea- and Environmental-Water', International Journal of Environmental Analytical Chemistry, 14: 1, 73 — 80

To link to this Article: DOI: 10.1080/03067318308071608

URL: http://dx.doi.org/10.1080/03067318308071608

Intern. J. Environ. Anal. Chem., 1983, Vol. 14, pp. 73–80
0306-7319/83/1401-0073 $06.50/0

Printed in Great Britain

An Analytical Method of Ultra-Trace Tellurium for Samples of Sea- and Environmental-Water†

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(*Received April 17*, 1982; *in final form August 10, 1982*)

This paper presents a method for the concentration of tellurium in sulfhydral cotton fiber. The mechanism of Te-Re catalytic polarographic behaviour has been studied. The optimal conditions of systems are proposed. An analytical procedure of preconcentration with sulfhydral cotton fiber and catalytic polarographic determination of ultra-trace tellurium is presented. This method exhibits good selectivity and is simple and easy. It is also one of the most sensitive analytical methods of tellurium at present. The procedure is demonstrated successfully for the determination of background levels of tellurium in a variety of natural water. This is the first reported determination of tellurium in sea water, filling a gap in the literature of oceanic geochemistry. It was found that the content of tellurium in South China sea water is 8×10^{-10} g/l, that in East China sea water is $4–7 \times 10^{-10}$ g/l.

KEY WORDS: Tellurium, polarographic catalytic wave, sulfhydral cotton fiber, sea water, preconcentration of tellurium.

INTRODUCTION

Tellurium is known to be a poisonous element to humans. In recent years, determination of trace tellurium has been given great attention in connection with the wide application of its compounds and/or with environmental pollution. The determination of ppb level of tellurium in waste water[1] and artificial water samples[2] by atomic-absorption spectrophotometry has been reported in the literature. As the tellurium content in natural waters is extremely low, there has not yet been reported

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†Presented at the 12th Annual Symposium on the Analytical Chemistry of Pollutants, Amsterdam, April 1982.

any sensitive analytical method for determination of its background value in various natural waters. In oceanic chemistry, data about tellurium content in sea-water are rather scarce.

This paper will summarize our investigation on the analytical method of preconcentration with sulfhydral cotton fiber (S.C.F.) and the catalytic polarographic determination of ultra-trace tellurium in water. This is the first time that the tellurium concentration in sea water in China has been reported.

EXPERIMENTAL

Reagents

All solutions were prepared from analytical-reagent (or G.R.) grade chemicals and twice-distilled water.

Standard tellurium solutions, (1000 ppm), were prepared by dissolving 1.251 g of tellurium dioxide in 50 ml of 6 N hydrochloric acid, and then diluting to 1000 ml with water; it was further diluted with water to give a concentration of 1 ppm or lower before use.

Standard rhenium (VII) solutions, (200 ppm), were prepared by dissolving NH_4ReO_4 in water.

Hydrochloric acid solutions, (6 N), were prepared by mixing 12 N HCl with water and passing through a tube with S.C.F. in order to remove tellurium from it.

For the preparation of S.C.F., see Reference[3].

Mixed solutions were prepared as follows: In a 100 ml of volumetric flask were added 30 ml of 6 N hydrochloric acid, 20 ml of 10% hydroxylamine hydrochloride, 0.8 ml of 200 μg/ml Re(VII) and 1 ml of 0.5% polyvinyl alcohol solution. The solution was diluted to the mark with twice-distilled water.

Apparatus

All polarograms were recorded with Model (883) d.c. Polarograph.

A capillary was used throughout this work with the following characteristics: $t = 6.0$ sec, $m = 0.00735$ g/6.0 sec., at 55 cm mercury pressure and -0.70 V applied voltage.

All potential values are referred to a large area Ag-Hg electrode. The absorption tube consisted of a glass tube ($\phi = 6$ mm, $L = 10$ cm) with a tapered end filled with the right amount of S.C.F. before analysis.

RESULTS AND DISCUSSION

1) The concentration of ultra-trace tellurium.

Experiments showed that the S.C.F. could adsorb quantitatively 5 ng tellurium from 1500 ml of water sample under the condition of 0.1–9 N of hydrochloric acid (Fig. 1), and that the absorbed tellurium on the S.C.F. could be washed quantitatively by 9–14.8 N of nitric acid (Fig. 2).

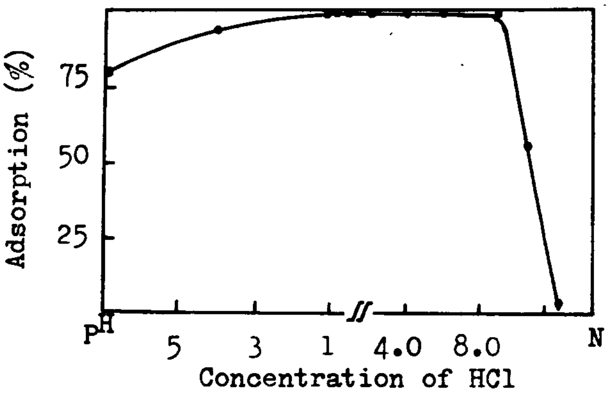

FIGURE 1 Adsorption curve of tellurium

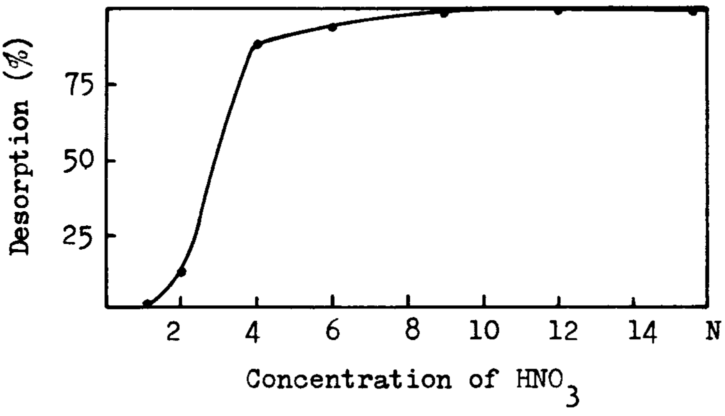

FIGURE 2 Desorption curve of tellurium

2) Investigation on the mechanism and the conditions for polarographic catalytic behaviour of tellurium.

We made detailed investigations and some improvements on the various conditions given in Reference[4] for the catalytic polarographic wave of tellurium-rhenium generated. It was found that the peak current of the catalytic polarographic wave was increased significantly by the presence of

Cl^- ion (Fig. 3) and that the presence of Na^+ ion would reduce the height of catalytic wave, while the addition of $SO_4^=$ ion shows no effect. It was proposed that the optimal media conditions of catalytic wave should be 2.8 M HCl, 2% $NH_2OH \cdot HCl$, 1.6 μg Re(VII)/ml and 0.005% polyvinyl alcohol. The sensitivity for the determination of tellurium is 9×10^{-11} M in this system. The shape of the catalytic polarographic wave was sharp in this system. The peak height was increased about 5000-fold in the presence of Re(VII) (see Fig. 4). The polarographic wave was proved to be a kinetic polarographic wave with adsorption by mercury column height and temperature and by the electrocapillary curve test. After controlled-potential electrolysis for three hours, the catalytic current was decreased two-fold. Therefore, a possible mechanism of polarographic catalytic wave was shown as follows:

$$\text{Te(IV)} \longrightarrow \text{Te(II)} \quad \text{electrode reaction}$$

$$\text{Te(II)} \xrightarrow[k]{ReO_4^-} \text{Te(IV)} \quad \text{chemical reaction}$$

Tellurium (IV) is formed easily as a complex (existing in the form of $TeCl_6^=$) in hydrochloric acid which is used as the supporting electrolyte and the complexing agent for tellurium as well. The sensitivity of catalytic polarographic wave in a HCl solution was higher relative to that in H_2SO_4 solution. Tellurium was reduced from a quadrivalent to a low-

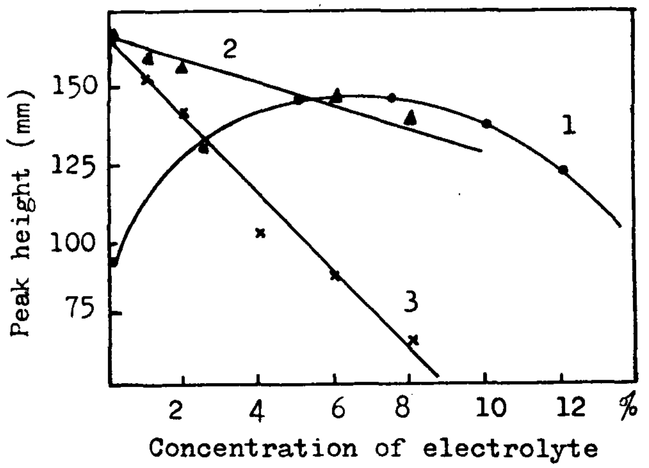

FIGURE 3 Effect of electrolyte concentration on peak height of tellurium (electrolyte: 1—NaCl, 2—K_2SO_4, 3—Na_2SO_4, Te: 1×10^{-9} g/ml S = 2).

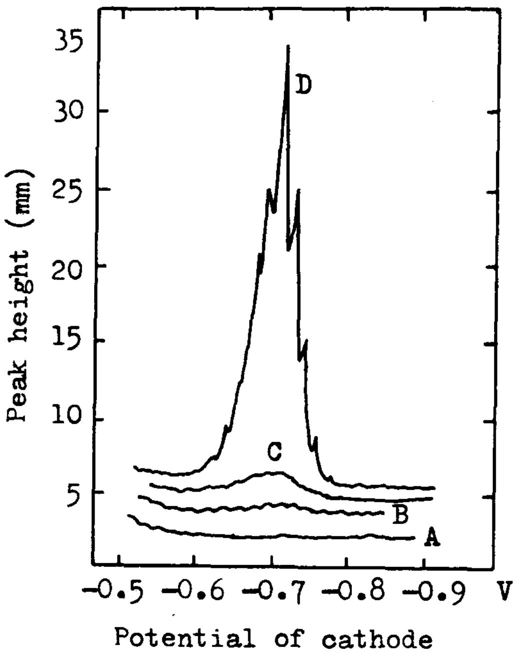

FIGURE 4 Polarographic catalytic wave of tellurium (S = 10, t = 22 C) A—2.8 N HCl, 2% NH_2OH 0.005% polyvinyl alcohol, B—A + Re(VII), C—A + Te(0.2 μg/ml), D—B + Te(1 ng/ml).

valent state (bivalent and/or elementary), and Te(II) transferred into Te(IV) and Te(0) by disproportional catalysis by the presence of ReO_4^- ion.[5] Te(0) was oxidized to Te(II) in the presence of ReO_4^- ion. Te(II) was again transferred into Te(IV) and Te(0). The tellurium (IV) regenerated was reduced again on the electrode. Thus, a continuous cyclic was formed. It was such a continuous recycle process that achieved the remarkable increase of the limiting current which was much larger than the diffusion-controlled wave expected. To add hydroxylamine hydrochloride in the presence of Re(VII) increased the catalytic current because it facilitated the chemical reaction process of low-valent tellurium oxidation to tellurium (IV). Hence the presence of certain amounts of hydroxylamine hydrochloride is of help for the increase of sensitivity. The rate constant for chemical reaction was calculated from the equation[6] of parallel catalytic wave:

$$\bar{i}_l/\bar{i}_d = 0.81\,(2K[0_x]t)^{1/2}$$

where:

$\bar{i}_l$ = catalytic current

$\bar{i}_d$ = diffusion current
K = rate constant for chemical reaction
$[0_x]$ = concentration of ReO_4^-(M)
t = time of mercury drop (sec.)

in which value K was derived ($K_{22^\circ C} = 7.2 \times 10^9$ L/Molar.sec.). K value is so large that this reaction proceeds rapidly. Thus the catalytic current produced in this system was particularly large.

3) Interfering test and analysis of artificial sea-water.

There were interferences for the polarographic determination when small amounts of As^{3+} and Sb^{3+} and large amounts of Mo(VI), Se(IV), Pt(IV), Bi^{3+}, V(V), Ti(IV) and Cd^{2+} (Te: Me < 1:300) were present. After sample preparation with S.C.F., only As, Pt, Se, Sb and Bi (20% absorbed) of those interferents were absorbed. But Sb and Bi absorbed could be reduced with 6 N hydrochloric acid, and the interference of As, Pt and Se could be eliminated through treatment of evaporation with HBr.

Tests show that there are no interferences from a large amount of usual ions and 1000-fold Sb^{3+}, As^{3+}, W(VI), Mo(VI), V(V), Se(IV), Pt(IV), Ti(IV) and Bi^{3+}, which meets the demand of determination of water samples.

In order to find the reliability of analytical method, we synthesized artificial sea water of Te (1.0 ng/L). The recovered amount of tellurium by this method was 1.1 ng/L, which proved that other elements in sea water do not interfere the determination.

4) Analytical procedure

a) Calibration curve

To different weights ($0.25 - 5 \times 10^{-8}$ g) of tellurium solution in the 25 ml volumetric flask was added 2.5 ml 9 M H_2SO_4, diluted to the mark with the mixed solution, shaken well and transferred to the polarographic cell and deaerate for 5 min. Instrumental settings were splitter(S) 2 or 4, compensator 10, and damping 3. The catalytic polarographic wave was recorded at −0.5− −0.9 V (vs. Hg) at 20°C. The height of the peak was measured and plotted against tellurium concentration (see Fig. 5). Blank assays were made in all experimental processes.

b) Analysis of water samples

The sea-water or environmental water samples were acidified with hydrochloric acid and filtered through 0.45 μm membrane. 2000 ml of filtered water samples were placed in a narrow mouthed holding bottle.

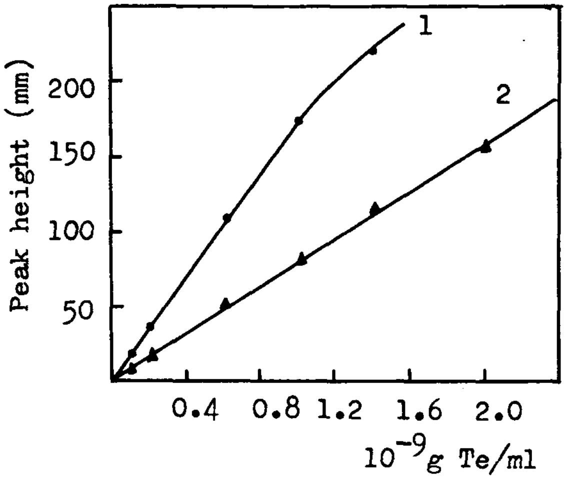

FIGURE 5 Calibration curves for tellurium determination (1—S = 2, 2—S = 4).

1000 ml of 6 N hydrochloric acid were added, shaken well and passed through the tube with 0.15 g of S.C.F. The samples adsorbed in the S.C.F. tubes washed with 20 ml of 6 N hydrochloric acid. The S.C.F. was removed from the tubes, the acid solution evaporated and the S.C.F. washed again with a small amount of distilled water. The tellurium adsorbed on S.C.F. was washed carefully in a small beaker (with 0.5 ml of 9.7 M sulfuric acid followed by 0.5 ml of perchloric acid) and finally washed with 3 ml of concentrated HNO_3 three times. The beaker was heated on low-temperature electric hot plate (the temperature is less than 120°C). When the smoke of $HClO_4$ appeared, 5 srops of HBr was added and evaporated until the $HClO_4$ stopped smoking. Then the temperature was increased until the H_2SO_4 smoked. After cooling, 5 ml of mixed solution were added and the polarographic determination was made. The height of the peak was measured and the content of tellurium of samples was determined from a calibration curve.

5) Analysis of water samples.

Results of analysis of a variety of water samples are shown in Table I. The relative standard deviation of this method is less than 10%. The recovery of tellurium in various water samples was 73–120%.

It was found that the content of tellurium in the South China sea-water was 8×10^{-10} g/L, and in the East China sea-water 4–7 $\times 10^{-10}$ g/L. Up to now, there may not have been any quantitative data of Te content for sea-water in the whole world, because of the lack of the reliable sensitive analytical method for ultratrace tellurium.[7] We determine quantitatively

TABLE I
Results of analysis for water samples

A variety of water samples	South China sea-water	East China sea-water (1)	East China sea-water (2)	Ming River water	Fuzhou running water	The hot spring ground water
The content (ng/L)	0.8	0.4	0.7	2.8	2.3	<0.3

The data of determination in Table I is an average measurement made more than twice.

the content of tellurium for sea-water, which fills the lack of data in oceanic geochemistry concerning tellurium. The data (10^{-10} g/L level) of this report for the content of tellurium in sea-water is 2 orders of magnitude less than the figure estimated in reference[8].

CONCLUSION

This paper presents a method for work on the concentration of tellurium with sulfhydral cotton fiber (S.C.F.). The mechanism of Te-Re polarographic catalytic wave was studied, the optimal condition of the system was proposed, and an analytical method of preconcentration with S.C.F. and catalytic polarographic determination of ultra-trace tellurium was described. This method is of good selectivity. It is easy to make use of, and is considered one of the most sensitive analytical methods of tellurium at present. It has been used successfully on determination of background value for a variety of natural waters. This is the first reported determination of tellurium for sea-waters, filling the blank of tellurium content in oceanic-geochemistry. The content of tellurium for the South China sea-water was found to be 8×10^{-10} g/L, that for the East China sea-water $4\text{–}7 \times 10^{-10}$ g/L, which is about 2 orders of magnitude less than the estimated figure reported in the literature for oceanic-geochemistry.

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