



# Spectrophotometric determination of trace amounts of tungsten in geological samples after preconcentration on Amberlite XAD-1180

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## Abstract

A method for the preconcentration of trace amounts of tungsten as its thiocyanate complex, using a column filled with Amberlite XAD-1180 resin, is proposed. After elution with a small volume of acetone, the analyte was determined spectrophotometrically with potassium thiocyanate and stannous chloride. The influence of several ions, as interferents, is discussed. The proposed method was applied to the determination of tungsten in geological samples with good analytical results, such as recoveries of 95% or above, relative standard deviations of 6% or below ( $n = 10$ ) and a detection limit of  $12 \mu\text{g l}^{-1}$ .

## 1. Introduction

The direct determination of tungsten in various matrices such as geological samples, steels, natural waters, etc. has presented some problems, due to the low tungsten content and large concentration of accompanying elements. Many preconcentration and separation methods have been used for the determination of tungsten at low concentrations, such as liquid–liquid extraction [1,2], adsorption [3] and ion exchange [4,5].

Up to now, a tin(III) chloride–thiocyanate method has been combined with a preconcentration and separation procedure for the determination of tungsten [6–10]. Columns filled with Amberlite XAD resin have been used for the preconcentration and separation of trace amounts of several metal ions from various matrices [11–13]. However, little work in this

field has been done using Amberlite XAD-1180 resin [14,15].

This paper describes a sorbent extraction system for the preconcentration of tungsten based on its solvent extraction as a thiocyanate complex. In this system, the sorption of the W(V)–thiocyanate complex is carried out by using Amberlite XAD-1180 resin. After elution, tungsten is determined spectrophotometrically. The procedure has been applied satisfactorily to the determination of tungsten in geological samples.

## 2. Experimental

### 2.1. Apparatus

A Hitachi 150-20 double-beam spectrophotometer equipped with a pair of 1 cm path length quartz cuvettes was used for the absorbance measurements. The determination of tungsten was performed at 400.0 nm.

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## 2.2. Reagents and solutions

All the chemicals used were of analytical grade, and aqueous reagents were prepared in doubly distilled, deionized water.

A 1000  $\mu\text{g ml}^{-1}$  stock solution of tungsten was prepared by dissolving an appropriate amount of sodium tungstate dihydrate in water and diluting it to 1000 ml. The stock solution was standardized gravimetrically by the tannic acid–phenazone method [16]. Appropriate standards and solutions of tungsten were prepared daily by dilution with water.  $\text{SnCl}_2$  solution (20% (w/v)) was prepared in concentrated HCl. KSCN solution (25% (w/v)) was prepared in water.

Amberlite XAD-1180 resin (particle size, 0.1–0.2 mm; Rohm and Haas Co.) was prepared using the reagents and the washing steps as reported previously [17].

## 2.3. Column preparation

An Amberlite XAD-1180 column, 10 cm long and 1 cm in diameter, containing about 400 mg of resin (about a 20 mm bed) was used for the experiments. The column was prepared by aspirating a water slurry of Amberlite XAD-1180 (400 mg) into the glass column. It was equilibrated with 10–15 ml of 3 M HCl solution containing 1.0 ml of 25% KSCN and 1.0 ml of 20%  $\text{SnCl}_2$ , after which the column was used in the preconcentration study.

## 2.4. Column preconcentration

The column method was optimized using 25–100 ml of model solution containing 40  $\mu\text{g}$  of tungsten. Solutions containing 0.2–5 ml of 25% KSCN and 0.2–5 ml of 20%  $\text{SnCl}_2$  were prepared in 0.5–10 M HCl solution. The resulting solutions were drawn through the column at a flow rate of about 3–5  $\text{ml min}^{-1}$  by vacuum. The column was then washed with the blank solution and the retained tungsten was eluted into a 25 ml beaker with 2–10 ml of acetone at a rate of 1–2  $\text{ml min}^{-1}$ . The eluate was evaporated to 0.5–1 ml on a hot plate, then cooled. The concentrated residue was transferred to a calibrated volumetric flask containing 1.5 ml of 25% KSCN and 1.5 ml of 20%  $\text{SnCl}_2$ , and the solution was made up to 5–10 ml with 3 M HCl solution. The tungsten concentration was determined spectrophotometrically as the thiocyanate complex at 400.0 nm [8].

## 2.5. Determination of tungsten concentration in geological samples

The geological samples were collected from Sorgun Yeni Çeltek Mine Quarry (Yozgat, Turkey). The decomposition procedure described by Welsch [18] was applied to the determination of the tungsten concentration in geological samples. The samples were ground and sieved to 80–100 mesh, 0.1–0.5 g amounts were weighed and transferred to 100 ml Teflon beakers, and 5 ml of concentrated nitric acid and 20 ml of concentrated HF were added to each beaker. The sample mixtures were evaporated to dryness, heated overnight at 125°C in a sand bath, and 2 ml of warm water and 8 ml of concentrated HCl were added to each residue and mixed. The mixtures were filtered through Whatman no. 42 filter paper, and 20 ml of water were added to each filtrate. The resultant solutions were drawn through the column as in the described procedure above.

## 3. Results and discussion

### 3.1. Effects of the reagents and hydrochloric acid concentration on the recovery of tungsten

The effects of the KSCN and  $\text{SnCl}_2$  amounts on the recovery of tungsten on Amberlite XAD-1180 resin were examined. The recoveries were quantitative (above 95%) in the range 0.5–5 ml of 25% KSCN and in the range 0.2–0.5 ml of 20%  $\text{SnCl}_2$  (Fig. 1).

The influence of the hydrochloric acid concentration on the retention of tungsten on Amberlite XAD-1180 resin is shown in Fig. 2. The highest sensitivity for tungsten was obtained in the HCl concentration range 2–9 M.

In all subsequent studies, 1.0 ml of 25% KSCN and 1.0 ml of 20%  $\text{SnCl}_2$ , as optimum amounts, were used. The concentration of the medium was made up to 3 M HCl with concentrated HCl.

### 3.2. Influences of eluent type and volume

The effects of the various eluents on the retention of tungsten on XAD-1180 resin was investigated. As can be seen in Table 1, elution with chloroform and diethyl ether was not quantitative. The recoveries of tungsten were quantitative when acetone, methanol, ethanol, *n*-butanol and *n*-propanol were used as eluent.

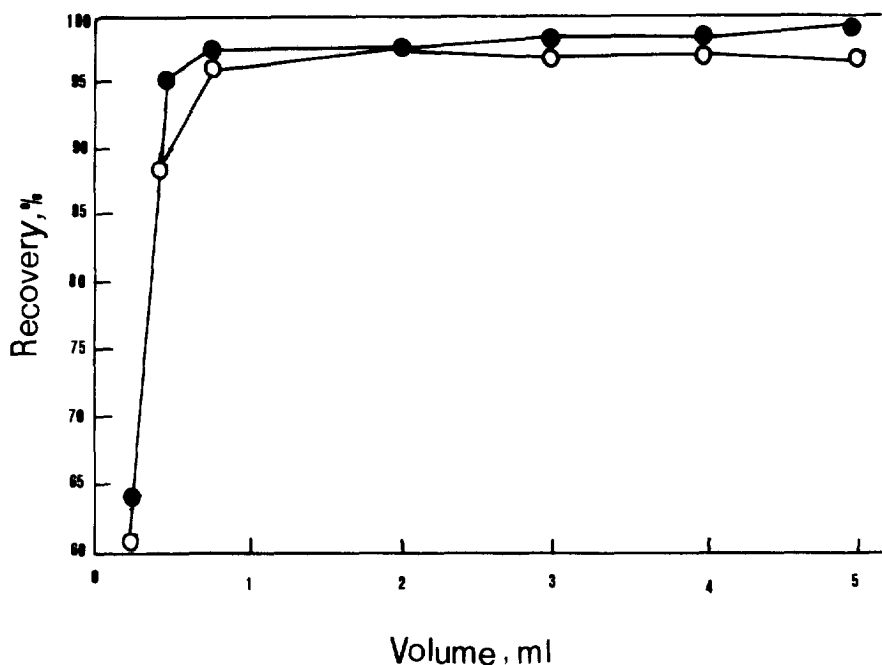


Fig. 1. Effect of the  $\text{SnCl}_2$  and  $\text{KSCN}$  amounts on the recovery of tungsten on Amberlite XAD-1180 resin ((●) ml of 20%  $\text{SnCl}_2$  and (○) ml of 25%  $\text{KSCN}$ ).

However, the evaporation of *n*-propanol and *n*-butanol is slower than that of acetone. The period of elution with methanol and ethanol is longer than that for the other eluents. As a result, acetone was selected as eluent in subsequent work.

The influence of the eluent volume on the recovery of tungsten was studied by using various volumes of acetone varying from 2 to 30 ml. The recoveries were quantitative in the range 2–20 ml. In the subsequent studies, 10 ml of eluent were used.

### 3.3. Effects of resin amounts and sample volume

The effect of XAD-1180 resin amounts on the recovery of tungsten was studied by varying the amounts of resin from 200 to 800 mg. Quantitative recoveries were obtained in the range 300–600 mg of the resin; as the optimum, 400 mg of Amberlite XAD-1180 resin were used. The same resin sample was used repeatedly for 300 sample analyses at least without loss of activity.

The effect of sample volume was examined with solutions containing 40  $\mu\text{g}$  of tungsten. Recoveries of the analyte concentrated into 2–10 ml of eluent from 50 to 500 ml sample volumes were found to be 97–100%. In this case, the highest preconcentration factor was found to be 250.

### 3.4. Calibration graph and detection limit

The calibration graph for a 100 ml sample was linear up to 200  $\mu\text{g}$  of tungsten. The detection limit, based on three times the standard deviation of the blank, was 12  $\mu\text{g l}^{-1}$  ( $n = 21$ ) and the relative standard deviation was 2% ( $n = 10$ ) at the 40  $\mu\text{g}$  of tungsten per 100 ml level.

### 3.5. Effects of foreign ions

The effects of foreign ions on the determination of tungsten were investigated. For these studies, different amounts of the ionic species were added to 40  $\mu\text{g}$  of tungsten determined by the standard procedure. The results are summarized in Table 2. The tolerance limits of the foreign ions were obtained with a relative error not greater than 5%.

The results in Table 3 show that the recoveries were unaffected when the solution contained chloride, sulfate, iodide, fluoride, sodium, magnesium and calcium ions. However,  $\text{Cu}^{2+}$ ,  $\text{Mo}^{6+}$  and  $\text{Fe}^{3+}$  ions interfere. The interference of copper was prevented by the addition of appropriate amounts of a 10% potassium ferricyanide solution [18].  $\text{Fe}^{3+}$  ions in the samples were completely reduced with 3 ml of 20%  $\text{SnCl}_2$ . Therefore, the interference effect of the  $\text{Fe}^{3+}$  ions was prevented. The concentrations

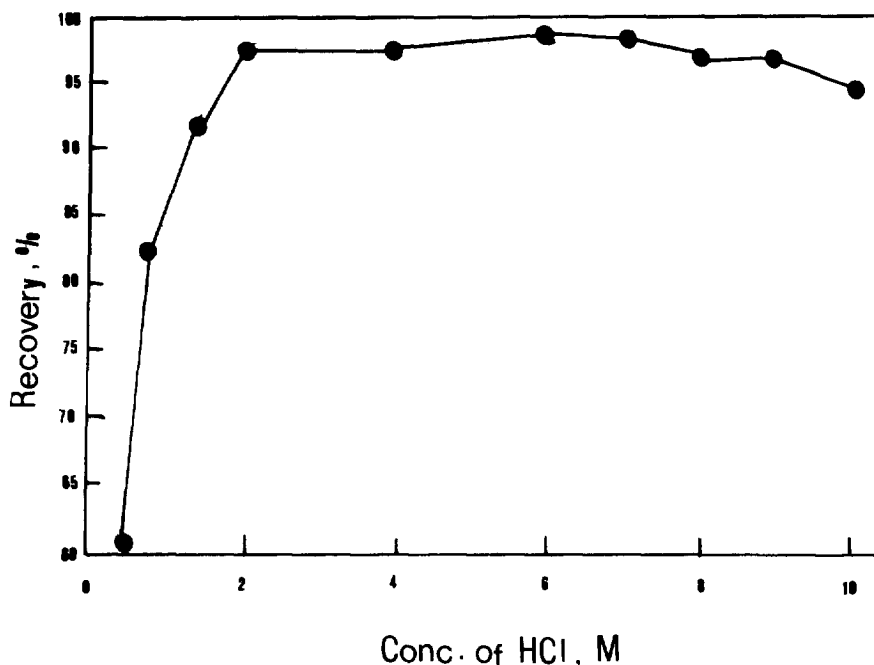


Fig. 2. Effect of the concentration of HCl on the recovery of tungsten on Amberlite XAD-1180 resin.

Table 1

Recoveries<sup>a</sup> of tungsten on Amberlite XAD-1180 with various eluents<sup>b</sup>

Eluent	Recovery (%)
Acetone	97 ± 1
Methanol	95 ± 3
Ethanol	96 ± 1
<i>n</i> -Butanol	96 ± 3
<i>n</i> -Propanol	99 ± 4
Chloroform	< 5
Diethyl ether	< 5

<sup>a</sup> *n* = 7.

<sup>b</sup> Eluent volume, 10 ml.

of Co<sup>2+</sup>, Zn<sup>2+</sup>, Bi<sup>3+</sup>, Cd<sup>2+</sup> and Mo<sup>6+</sup> ions in the geological samples were found to be within their tolerance limits.

### 3.6. Tungsten content of geological samples

The method was applied to the determination of tungsten in geological samples collected from the Mine Quarry (Yozgat, Turkey). The results are given in Table 3. The determination of the tungsten content in the samples was also performed using a well-known and accepted extraction method [9]. There are no significant differences between the concentration values obtained by both methods at the 95% con-

Table 2

Tolerance limits of foreign ions for the recovery of tungsten on Amberlite XAD-1180<sup>a</sup>

Ion	Added as	Tolerance limit (µg ml <sup>-1</sup> )
Ca <sup>2+</sup>	CaCl <sub>2</sub>	2500
Na <sup>+</sup>	NaCl	10000
Mg <sup>2+</sup>	MgCl <sub>2</sub>	1000
SO <sub>4</sub> <sup>2-</sup>	Na <sub>2</sub> SO <sub>4</sub>	1000
NO <sub>3</sub> <sup>-</sup>	NaNO <sub>3</sub>	500
F <sup>-</sup>	NaF	250
Fe <sup>3+</sup>	FeCl <sub>3</sub>	50
Cu <sup>2+</sup>	CuCl <sub>2</sub>	5
Mo <sup>6+</sup>	Na <sub>2</sub> MoO <sub>4</sub>	5
Co <sup>2+</sup>	Co(NO <sub>3</sub> ) <sub>2</sub>	15
Zn <sup>2+</sup>	Zn(NO <sub>3</sub> ) <sub>2</sub>	50
Bi <sup>3+</sup>	Bi(NO <sub>3</sub> ) <sub>3</sub>	25
Cd <sup>2+</sup>	Cd(NO <sub>3</sub> ) <sub>2</sub>	50

<sup>a</sup> Sample volume, 250 ml; *n* = 4.

fidence level. However, better precision is obtained with the column method.

## 4. Conclusion

The Amberlite XAD-1180 column method was applied to the determination of the tungsten concentration in geological samples, and accurate results were obtained. The results obtained using this column method and the extraction method are in agreement. The

Table 3

Concentration of tungsten in geological samples collected from the Sorgun Yeni Çeltek Mine Quarry (Yozgat, Turkey)

Depth (m)	Concentration of tungsten ( $\mu\text{g g}^{-1}$ ) <sup>a</sup>			
	Column	RSD (%)	Extraction	RDS (%)
60	195 ± 10	5.13	187 ± 14	7.51
100	176 ± 10	5.68	162 ± 12	7.36
170	311 ± 17	5.51	316 ± 25	7.91
220	224 ± 13	5.83	220 ± 12	5.45
220 <sup>b</sup>	218 ± 5	2.29	222 ± 11	5.01
360	479 ± 19	4.01	489 ± 36	7.39

<sup>a</sup>  $n = 7$ ;  $P: 0.95$ ;  $\pm t_{.5} \sqrt{\bar{n}}$ .

<sup>b</sup> Samples were collected from two different zones at a depth of 220 m.

proposed method can easily be used for the determination of tungsten in industrial samples such as alloys and steel samples, etc.

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