

## Use Of Differential Pulse Cathodic Adsorptive Stripping Voltammetric Method For The Simultaneous Determination Of Trace Amounts Of Cadmium and Zinc

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### Abstract

A selective and sensitive method for determination of cadmium and zinc is presented. The method is based on adsorptive accumulation of the complexes of Cd (II) and Zn (II) ions with 4-amino-5-methyl-2,4-dihydro-3H-1,2,4-triazol-3-tion (MMTT) onto hanging mercury drop electrode (HMDE), followed by reduction of the adsorbed species by voltammetric scan using differential pulse modulation. The ligand concentration, pH, potential and time of accumulation, scan rate and pulse height were optimized. Under the optimized conditions, a linear calibration curve was obtained for the concentration of Cd (II) and Zn (II) in the range of 5-450 and 5-850 ng/ml, respectively, with a detection limit of 1.7 ng/ml Cd (II) and 1.3 ng/ml Zn (II). The ability of the method was evaluated by analysis of cadmium and zinc in water and alloy samples.

**Keywords:** Cathodic stripping voltammetry; Cadmium; Zinc; MMTT

### Introduction

The determination of heavy metals such as cadmium and zinc is important because they may be toxic through biomagnifications, or to investigate their geochemistry [1]. The pollution of these ions is one of the most serious environmental problems because of their stability in contaminated site and complexity of mechanism in biological toxicity. They can be accumulated in the body and greatly threaten the health of human [2-5]. Metallic ions of cadmium and zinc frequently exist together in many real environmental and food samples. It is necessary to determine these ions simultaneously in most instances [6]. The most commonly used methods for the determination of various metal ions are atomic absorption spectrometry (AAS) [7,8], atomic emission spectrometry (AES) [9] and mass spectrometry (MS). However, these techniques have

some disadvantages, such as complicated operation, high cost of maintenance, expensive apparatus and requiring well-controlled experimental conditions.

For the above reason electrochemical method, such as stripping voltammetry (SV), is one of the most favorable techniques for the determination of heavy metal ions, including cadmium (II) and zinc (II), because of its low cost, high sensitivity, easy operation and the ability of analyzing element speciation. Stripping voltammetry comprises a variety of electrochemical approaches, having a step of pre-concentration onto the electrode surface prior to the voltammetric measurements. The major advantage of SV compared with direct voltammetric measurement and other analytical techniques is the pre-concentration factor. Anodic stripping voltammetry (ASV) that is the most popular stripping voltammetric technique is an effective technique for the determination of trace amounts of metal ions [10,11]. Although anodic stripping voltammetry is a powerful tool for the determination of trace amounts of these two important elements but the application of ASV for the determination of analytes in complex sample matrices is complicated because of the adsorption of interfering components onto the electrode surface with the result that electrode activity is lost and non-reproducible results are obtained. However the selectivity and sensitivity have further been also improved based on adsorption rather than electrolytic accumulation. Stripping analysis following adsorptive accumulation of metal chelates is becoming a widely accepted analytical tool. Several adsorption voltammetric methods have been reported for the determination of Cd (II) and Zn (II) with different reagents [12-16]. These methods either have short linear dynamic range or suffer from much interference.

The present study describes a new adsorptive stripping procedure for simultaneous determination of trace amount of cadmium and zinc by using of MMTT as a complexing agent. The method relies on the effective accumulation of the Cd (II) and Zn (II) complexes with MMTT onto the hanging mercury drop electrode. This method has large dynamic range, low detection limit and is able to determine cadmium and zinc in different real samples.

## **Experimental**

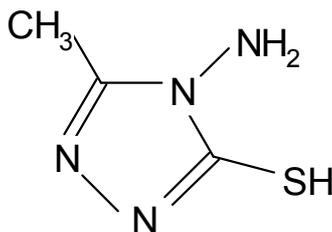
### **Apparatus.**

A Metrohm 746/747 VA processor was used for differential pulse voltammetry, with a three-electrode system consisting of a hanging mercury drop electrode (HMDE) as the working electrode, an Ag/AgCl (saturated KCl) reference electrode and a platinum counter electrode. All potentials reported were referred to the Ag/AgCl electrode. pH measurements were performed with a Metrohm 691 pH meter using a combined glass electrode. A Varian AA-50 atomic absorption spectrometer equipped with cadmium and zinc hollow cathode lamps was used for atomic absorption measurements.

### **Reagents**

All aqueous solutions were prepared with doubly distilled water. The stock solutions of Cd (II), 1000 mg/L were prepared by carefully weighting solid cadmium nitrate and zinc nitrate (Merck) in distilled water in two 100-ml volumetric flasks.

The ligand of 4-amino-5-methyl-2,4-dihydro-3H-1,2,4-triazol-3-tion (MMTT) was synthesized and purified according to a previously reported procedure [17]. A solution of  $1.0 \times 10^{-3}$  M MMTT was prepared by dissolving 0.0130 g of the compound in ethanol. The molecular structure of the MMTT is shown in Fig. 1.



**Fig. 1.** Structural formula of MMTT.

Tris buffers were prepared by mixing appropriate amount of tris(hydroxymethyl)-aminomethane, 0.1 M, and hydrochloric acid, 0.1 M, in different 100-ml volumetric flasks.

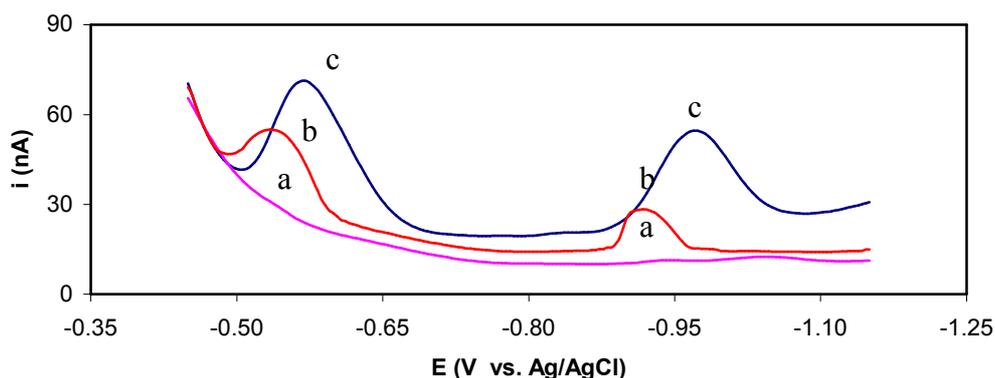
### Procedure

Ten milliliters of the supporting electrolyte solution (Tris buffer, pH 9.5) containing  $2.0 \times 10^{-5}$  M MMTT was transferred to the electrochemical cell and purged with nitrogen for 4 min. An accumulation potential of -0.1 V vs. Ag/AgCl was applied to a fresh mercury drop, while the solution was stirred, for an accumulation time 10 s. After the accumulation step was finished, the stirring was stopped, and after equilibration for 10 s, the differential pulse voltammogram was recorded from -0.45 to -1.15 V with a potential scan rate of 10 mV/s and pulse amplitude of 50 mV. After obtaining the background voltammogram, aliquots of cadmium and zinc standard solution were introduced into the cell and the obtained solution was deoxygenated with nitrogen gas for 1 min. Then a differential pulse voltammogram was recorded according to described procedure to give the sample peak current. All experiments were carried out at room temperature.

### Results and Discussions

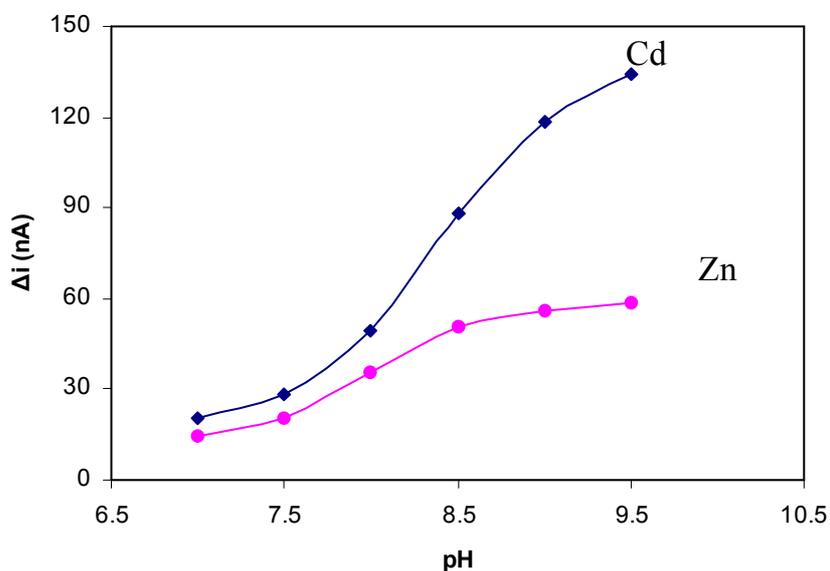
Preliminary experiments were carried out to identify the general features, which characterize the behavior of the Cd- and Zn-MMTT systems on mercury electrode. Fig. 2(a) displays differential pulse voltammograms of  $2.0 \times 10^{-5}$  M MMTT solution at pH 9.5 (Tris buffers) after 10 s accumulations at -0.1 V. In Fig. 2(b) the voltammogram of a solution containing 50 ng/ml of cadmium and 200 ng/ml of zinc in the absence of ligand under similar conditions is shown. The voltammogram of the mixture of  $2.0 \times 10^{-5}$  M MMTT and 25 ng/ml of Cd and 100 ng/ml of Zn under the same conditions is also shown in Fig. 2c. As can be seen in Fig. 2, the sensitivity of cadmium and zinc reduction currents enhanced due to the addition of MMTT to the solution because of adsorption properties of Cd-and Zn-MMTT complexes on the HMDE. These responses increased linearly with increasing metal concentrations. The peak currents increased with increasing accumulation time before the potential scan. By adding small amount of surfactants such as Triton X-100, and sodium dodecyl sulfate strongly suppressed the peak currents. In addition, the influence of scan rate showed that the peak currents increase with potential scan rate from 2 to 10 mV/s. These observations indicate that the metal-MMTT complexes were strongly adsorbed on mercury electrode surface.

Various experimental parameter affecting the sensitivity of Cd (II)-MMTT and Zn (II)-MMTT cathodic stripping response, were investigated.



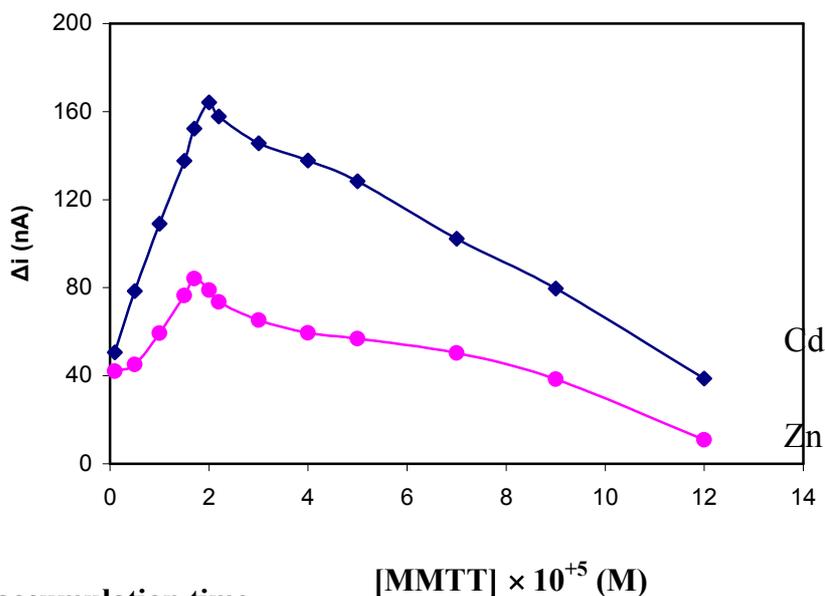
### Influence of supporting electrolyte and pH

Preliminary experiments were carried out with different types of buffers such as acetate, phosphate, citrate, borate, Phthalate, Britton-Robinson, ammonia-ammonium and Tris. The results showed that the peaks shape for cadmium and zinc were improved in the presence of Tris buffer solution. Therefore, Tris buffer was used for optimization of pH. The influence of pH on the cathodic stripping peak currents of cadmium and zinc was studied in the pH range of 7.0-9.5 (Fig.3). The results show that the peak currents for cadmium and zinc increase with increasing the pH. This phenomenon is due to the enhanced complexing ability of MMTT in large pH values. Thus, pH of 9.5 was adopted for further studies.



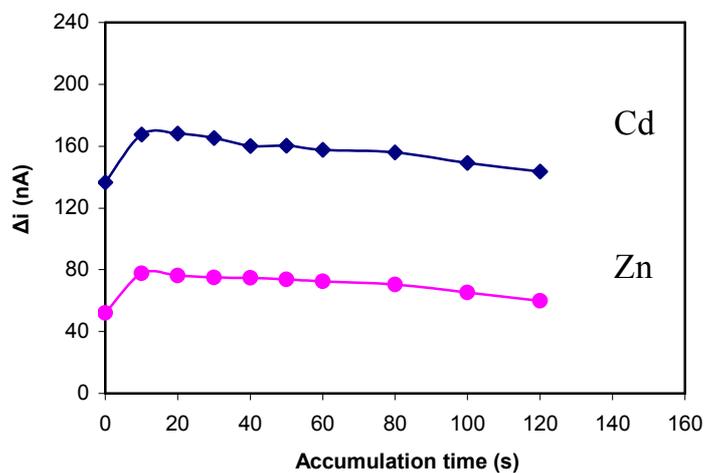
### Influence of MMTT concentration

The influence of MMTT concentration on the sensitivity of proposed method was also studied. The obtained results (Fig. 4) show that the cathodic stripping peak currents of Cd- and Zn-MMTT complexes increased with increasing the MMTT concentration up to about  $2.0 \times 10^{-5}$  M, leveling off at higher concentrations. This is due to the competition of MMTT with Cd- and Zn-MMTT complexes for adsorption on the HMDE. So, an optimum MMTT concentration of  $2.0 \times 10^{-5}$  M was selected for further experiments.



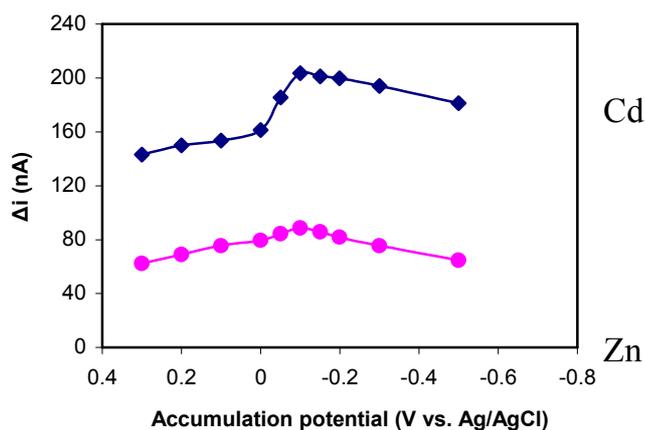
**Influence of accumulation time**

The effect of the accumulation time on the stripping peak currents for Cd and Zn in the range 0-120 s is illustrated in Fig.5. The peak currents increased initially with increasing preconcentration time up to 10 s and at higher preconcentration times the plots for both metals started to level-off slowly as the equilibrium surface concentration of the adsorbed complexes was approached. Therefore, an accumulation time of 10 s was selected for further investigations.



**Influence of accumulation potential**

The effect of the accumulation potential on the peak heights on Cd and Zn was studied in the range from 0.3 to -0.5 V and is shown in Fig. 6. The results show that the peak currents for cadmium and zinc increased up to preconcentration potential of -0.1 V, whereas for more negative potential values the peak height decreased gently. Thus a preconcentration potential of -0.1 V was selected as optimum value for further studies.

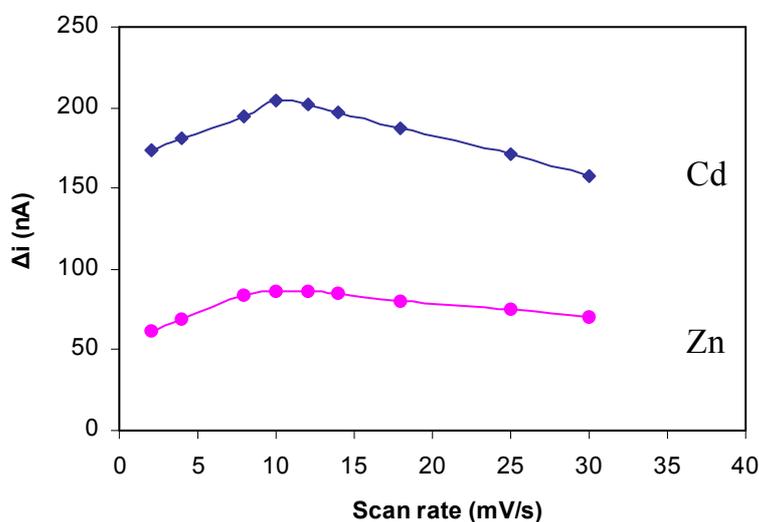


### Influence of pulse height

The dependence of peak currents on the pulse height in the optimal conditions was also investigated. The peak currents of cadmium and zinc increased with increasing pulse heights in the range from 20 to 100 mV. Due to the improvement of peak shape for both metal ions, the pulse height of 50 mV was selected for further studies.

### Influence of scan rate

Fig. 7 depicts the effect of scan rate on the stripping peaks of Cd and Zn in the optimal conditions that described before. The results show that the peak heights for both Cd and Zn increase nearly from 2 to 10 mV/s and in larger scan rates the sensitivity decreases. Therefore, a scan rate of 10 mV/s was selected.



### Linear range, detection limit and precision

Using the optimized conditions ( $2.0 \times 10^{-5}$  M of MMTT, pH 9.5, an accumulation potential of -0.1 V and 10 s accumulation time) the calibration graphs were found to be linear in the concentration range of 5-450 and 5-850 ng/ml for cadmium and zinc, respectively. The correlation equations for the dependence of cadmium and zinc peak currents on their concentration are  $\Delta i = 0.10C + 15.78$  ( $r^2=0.9988$ ) for  $\text{Cd}^{2+}$

concentration and  $\Delta i = 0.38C + 9.67$  ( $r^2=0.9993$ ) for  $Zn^{2+}$  concentration, where C is concentration of metal ions in ng/ml and  $\Delta i$  is the peak current vs. nA.

A detection limit (the blank signal plus three times of its standard deviation) of 1.7 ng/ml Cd (II) and 1.3 ng/ml Zn (II) was obtained.

Repeated voltammograms after 10 s accumulation time showed that the relative standard deviation for 30 and 60 ng/ml cadmium is 2.7% and 2.9% ng/ml and for 20 and 30 ng/ml zinc is 3.1% and 2.9% ng/ml, respectively.

#### Interferences studies.

Two major sources of interference were investigated. First, surfactants are the most serious interference in stripping analysis. Triton X-100 was used to simulate the effect of a non-ionic surfactant. Adding of 4  $\mu\text{g/ml}$  Triton X-100 to the solution containing 50 ng/ml Cd and Zn, completely suppressed their peaks. In addition, metal ions can also interfere (the criterion for interference was a 5% error in the peak heights of Cd and Zn) with the measurement by complexing competitively with MMTT or by production reduction peaks that overlap with or even completely suppress, the Cd and Zn peaks. A number of metal ions and anions that could potentially interfere were examined (Table 1). The results show that the method is free from much interference of foreign ions.

**Table 1:** Interference study for cadmium and zinc determination

Species	Tolerance limit $W_{\text{ion}}/W_{\text{Cd(II)}}$	Tolerance limit $W_{\text{ion}}/W_{\text{Zn(II)}}$
$K^+$ , $Na^+$ , $Cs^+$ , $HCO_3^-$ , $I^-$ , $Br^-$ , $Cl^-$ , $WO_4^{2-}$ , $N_3^-$ , $ClO_3^-$ , $ClO_4^-$ , $NO_3^-$ , $NO_2^-$ , $SO_4^{2-}$ , $S_2O_3^{2-}$ , $OAC^-$ , $Al^{3+}$ *	1000	1000
Hg(II)	1000	50
Pb(II)	500	1000
$BrO_3^-$	500	500
Mn(II)	500	100
$IO_3^-$	500	50
$F^-$	250	250
$Ca^{2+}$	250	100
$Sr^{2+}$ , $Ba^{2+}$	250	50
$CO_3^{2-}$	100	250
$Ni^{2+}$ , $SCN^-$	100	100
$Mg^{2+}$	100	50
$Co^{2+}$	50	20
Fe(III)	50	10
$Cu^{2+}$	20	250
$CN^-$	20	50
Pd(II)	10	100
Fe(II), Ce(IV)	10	10
Rh(III)	5	20

\*After adding 40  $\mu\text{g/ml}$  F<sup>-</sup>.

### Applications

The method was applied to natural water sources such as tap water, spring water and well water for determination of cadmium and zinc (Table 2). The proposed method was also used to determine zinc in a standard reference aluminum alloy material (NBS SRM 85b) (Table 2). In order to eliminate matrix effects, standard addition method was used. The alloy was dissolved according to Cantle [18]. The samples also were analyzed for cadmium and zinc contents by atomic absorption method. The utility of the developed method was tested by determining cadmium and zinc in several synthetic mixtures (Table 3). The results obtained by the proposed method show good recoveries and reveal the capability of the method for determination of cadmium and zinc in real samples.

**Table 2:** Determination of cadmium and zinc in natural water and alloy samples.

Sample	Added (ng/ml)		Found by AAS (ng/ml)		Found by proposed method (ng/ml)		% Recovery	
	Cd	Zn	Cd	Zn	Cd	Zn	Cd	Zn
Tap water	–	–	1.80( $\pm 0.08$ ) <sub>a</sub>	97.4( $\pm 3.9$ )	1.88( $\pm 0.07$ ) <sup>b</sup>	–	104.4	–
	40.0	40.0	–	–	40.6( $\pm 1.7$ )	138( $\pm 6.0$ )	97.0	101.5
	40.0	70.0	–	–	41.3( $\pm 1.5$ )	165.0( $\pm 6.4$ )	98.8	96.6
Spring water	–	–	–	151.5( $\pm 5.8$ )	–	–	–	–
	30.0	30.0	–	–	28.8( $\pm 1.4$ )	180.6( $\pm 5.9$ )	96.0	97.0
	60.0	60.0	–	–	58.9( $\pm 1.9$ )	212.4( $\pm 7.6$ )	98.2	101.5
Well water	–	–	–	842.1( $\pm 42.9$ )	–	–	–	–
	40.0	40.0	–	–	41.8( $\pm 2.1$ )	883.4( $\pm 28.3$ )	104.5	103.2
	40.0	60.0	–	–	40.7( $\pm 1.6$ )	899.8( $\pm 36.9$ )	101.8	96.2
NBS SRM 85b <sup>c</sup>	–	–	–	–	–	0.038( $\pm 0.001$ ) <sup>c</sup>	–	95.0

Number in parenthesis is the standard deviation for four replicate measurements.

<sup>a</sup>After 100-fold preconcentration.

<sup>b</sup>After 10-fold preconcentration.

<sup>c</sup>The composition (%W/W) of the aluminum alloy (NBS SRM 85b) was 93.097% Al, 0.61% Mn, 0.18% Si, 3.99% Cu, 0.084% Ni, 0.211% Cr, 0.006% V, 0.022% Ti, 0.019% Ga, 0.24% Fe, 0.021% Pb, 1.49% Mg and 0.040% Zn. <sup>c</sup> %W/W

**Table 3:**Determination of cadmium and zinc in synthetic mixtures.

Sample	Added (ng/ml)		Found (ng/ml)		Recovery (%)	
	Cd	Zn	Cd	Zn	Cd	Zn
1	30.0	30.0	28.4(±0.9)	29.1(±1.1)	94.7	97.0
2	60.0	90.0	62.0(±2.2)	91.9(±3.5)	103.3	102.1
3	90.0	150.0	90.7(±2.4)	156.6(±6.7)	100.8	104.4
4	120.0	90.0	124.1(±4.1)	87.7(±2.4)	103.4	97.4
5	120.0	210.0	116.6(±3.6)	205.4(±10.5)	97.2	97.8
6	150.0	270.0	156.2(±5.9)	260.3(±9.1)	104.1	96.4

Number in parenthesis is the standard deviation for four replicate measurements.

### Conclusions

The adsorption of Cd (II)-MMTT and Zn (II)-MMTT complexes on mercury electrode can be utilized for simultaneous determination of trace amounts of cadmium and zinc by adsorptive stripping voltammetry. This new method offers a practical potential for trace determination of cadmium and zinc, with high selectivity and sensitivity, simplicity and speed relative to other methods. This method was successfully applied for determination of Cd and Zn in real samples such as water and alloys.

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