Anodic Stripping Voltammetric Analysis of Trace Metal Ions of Pb, Cd, Cu and Zn in Tap Water

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ABSTRACT. Lead, cadmium, copper and zinc in part-per-billion (ppb) levels in laboratory tap water were determined by differential pulse anodic stripping voltammetry (DPASV). Triammonium citrate (0.2 M) was used as a supporting electrolyte. Differential pulse anodic stripping voltammograms for samples prior to and after spiking were recorded in the potential range − 1.2 to 0.0 volts by a microprocessor-controlled polarographic analyser. The indicator electrode used was static mercury drop electrode (SMDE) combined with Ag/AgCl (KCl sat.) reference electrode and a platinum auxiliary electrode. The results obtained by adopting standard additions method showed relative standard deivations less than 10%.

Recent concern about heavy metal contamination and its potential danger has lead to an increasing need to monitor trace levels in various waters. X-ray fluorescence spectrometry and flameless atomic absorption spectrometry (FAAS) are among the techniques currently used for trace metal analysis, Pinta (1978). At concentration levels such as is present in water, FAAS is the technique widely used in quality control of water. However, several electroanalytical procedures for the determination of toxic trace elements in a variety of matrices are based on polarography and voltammetry, Almestrand *et al.* (1986) and Nelson (1985).

In the Gulf Area and particularly in the Kingdom of Saudi Arabia considerable efforts are made to improve the quality of water for drinking or otherwise. It is the aim of the authors to apply (DPASV) technique for determination of trace levels of Pb, Cd, Cu and Zn in tap water to demonstrate the capability of this technique in the quantitation of low levels of heavy metals some of which are detrimental to health. The technique may be used on routine basis for

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quality control of water. Large number of samples may be handled conveniently due to partial automation of the analysis.

Booth *et al.* (1970), Colovos *et al.* (1974), Schneidman *et al.* (1982) and Miwa *et al.* (1972) demonstrated the utility of stripping analysis. A recent review by Florence (1986) outlined the successful application of stripping voltammetry for trace metal speciation in waters. Among the notable publications pertaining to the employment of stripping voltammetry in trace metals analysis, are the works by Wang *et al.* (1984), Locatelli *et al.* (1986), Lexa (1986), Mannio (1984) and Kiekens *et al.* (1984).

The sensitivity of (DPASV) is attributed to (i) the deposition step, in which the trace metals are preconcentrated onto the working electrode. This step is followed by the stripping (measurement) step, in which the electrode potential is scanned in the anodic direction, the resulting response (stripping voltammogram) produces current peaks, whose location on the potential scale characterizes the metal ion, and whose peak height (or peak area) is proportional to the concentration of the metal ion in the sample solution (ii) absence of the residual current which limits the sensitivity of the dropping mercury electrode.

The results obtained by applying (DPASV) indicate that the method is reproducible and is convenient to use for quality control of trace levels of Pb, Cd, Zn and Cu in water.

Experimental

(i) Reagents

All solutions should be prepared fresh daily and should not be stored. All the glassware should be soaked, preferably overnight in 6 M HNO_3 and rinsed several times with deionised water (triply distilled water).

Stock solutions of lead, cadmium, copper and zinc each 100 ppm were prepared fresh daily from standards of high purity Fluka AG, Chemische Fabrik CH-9470 using triply distilled water of electric conductivity less than 0.1 μS cm^{-1}.

Triammonium citrate supporting electrolyte (0.2 M).

Triammonium citrate (2.0 M) analytical reagent was dissolved in triply distilled water and purified by controlled-potential electrolysis at - 1.5 V for 24 hrs.

Water samples

Collected from tap water after letting the water run for 5 min, and kept in pyrex glass cleaned before-hand as explained previously.

Nitrogen gas

Used for purging to drive oxygen (electro-active) - purity $(W(N_2)) = 0.9999$.

(ii) Apparatus

Measurements were made, Schneidman *et al.* (1982), on a micro-processor-based Princeton Applied Research Model 384 polarographic analyser system, Princeton, N.J., U.S.A. The polarographic analyser is attached to static mercury drop electrode model 303 and digital plotter model DMP-2G, Houston Instrument, Austin, Texas. The operating parameters shown in Table (1) are programmable. The micro processor controls each step of the analysis. After completion of the analysis, the instrument normalizes the data and the digital plotter produces the measured curve with all the peaks labeled. The stirring operation during deposition was automated by a model 305 stirrer accessary.

Table 1. "Voltammetric Parameters"

Voltammetric mode	Differential pulse anodic stripping voltammetry, modulation amplitude 50 mV.
Indicator electrode	SMDE
Reference electrode	Ag/AgCl (KCl sat.)
Initial voltage	-1.2 V.
Final voltage	0.0. V.
Mercury drop size	Small
Purge time	5 min.
Deposition time	60 sec.
Scan rate	2 mV sec^{-1}.
Method of evaluation	Standard additions.

Procedure

Key the parameters in Table (1) to the analyser. Mix 1 ml of triammonium citrate and 9 ml of water sample. Transfer into the polarographic vessel. Purge with pure nitrogen for 5 min. Press run button and wait until the digital plotter completes scanning according to the instructions given by the analyser in the voltage range − 1.2 V to 0.0 V. Press playback button to obtain the recorded differential pulse stripping voltammogram by the digital plotter. Spike the sample with 100 µl of the standard solution containing 10 ppm of each metal cation. Purge with nitrogen and repeat as before to obtain a new voltammogram. The concentration of each metal will be worked out and printed. Dispense a fresh SMDE and introduce 10 ml of solution prepared as before in the polarographic

vessel. Repeat the procedure starting from "purge with pure nitrogen for 5 min. ..." Make nine runs and calculate the means and the relative standard deviations.

The following precautions are necessary

1. Care should be taken to avoid entrapped air in the mercury capillary since this results in change of size of the drop and hence erroneous results.
2. The reference electrode should be checked occasionally for clogging.
3. Stirring the solution during the deposition step is recommended to ensure uniform and reproducible concentration gradient at the electrode.
4. There can be interferences or cell-to-cell variation and the standard additions method is recommended to use.

Results and Discussion

Anodic stripping voltammetry and cathodic stripping voltammetry are inherently very sensitive voltammetric techniques used in environmental analysis comparable with FAAS (Bond, 1980). Many experimental parameters should be controlled in order that reproducible results are obtained. One important parameter is the deposition time during which the decomposition potential is applied. For very low levels of trace metals, the longer the decomposition time, the greater is the sensitivity since metals accumulate onto the mercury drop. However, it was observed that, Barendrecht (1967), stripping voltammetry using (SMDE) could be complicated by intermetallic formation such as $Cu - Zn$ and $Cu - Cd$ inside the mercury drop with the result that peaks might be shifted and/or suppressed.

Preliminary investigation showed that deposition time of 60 sec at -1.2 V was optimum since reproducible peaks were obtained (Fig. 1). At the applied potential of -1.2 V, Pb^{++}, Cd^{++}, Cu^{++} and Zn^{++} are reducible at SMDE, and in a single run in the anodic direction four peaks were obtainable in one voltammogram (Fig. 1).

Accurate analytical results require that the SMDE be of constant volume since the current increases with the size of the drop. The reproducibility of a small drop size of (SMDE) was tested by recording repetitive differential pulse stripping scans using solutions of 100 ppb Cd^{++} in 0.1 M $-$ KCl. A new drop was dispensed for each evaluation. The relative standard deviation obtained was 4.85% indicating good reproducibility. However, for medium and large drop size there was difficulty in keeping the drop hanging when stirring during deposition time.
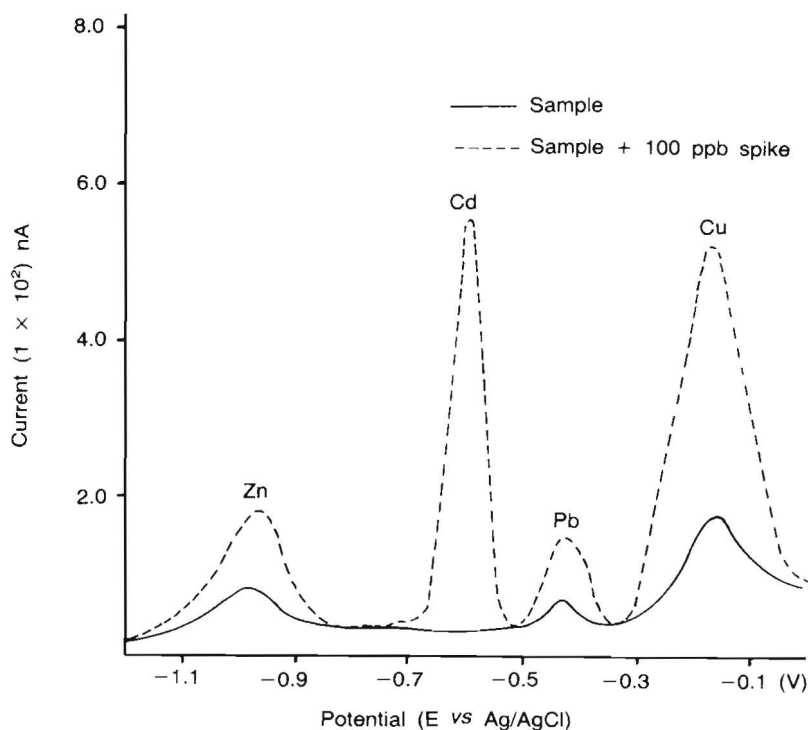
Fig. 1. Typical anodic stripping voltammogram for Pb, Cd, Cu and Zn.

Fig. 2 represents typical differential pulse anodic stripping voltammograms for Pb, Cd, Cu, and Zn in triammonium citrate supporting electrolyte. The voltammograms were recorded for the metal ions in the water samples before and after spiking; and evaluation was carried out with standard additions method. Nine replicate measurements were made. The results shown by Table (2) indicate a relative standard deviation less than 10%.

Since Pb, Cd, Cu and Zn ions (and possibly other heavy metals) are generally present in very low concentrations in water, their determination is extremely susceptible to problems of contamination and/or loss during storage. Potential errors may accrue from sampling, reagents used and/or adsorption of metal ions onto the walls of the container, Laxen *et al.* (1981).

As a conclusion DPASV offers an encouraging rapid method for the determination of trace levels of Pb, Cd, Cu and Zn in water provided that necessary precautions are taken. If proper measures are taken, the DPASV can be applied successfully for the quantiation of other heavy metals as well.
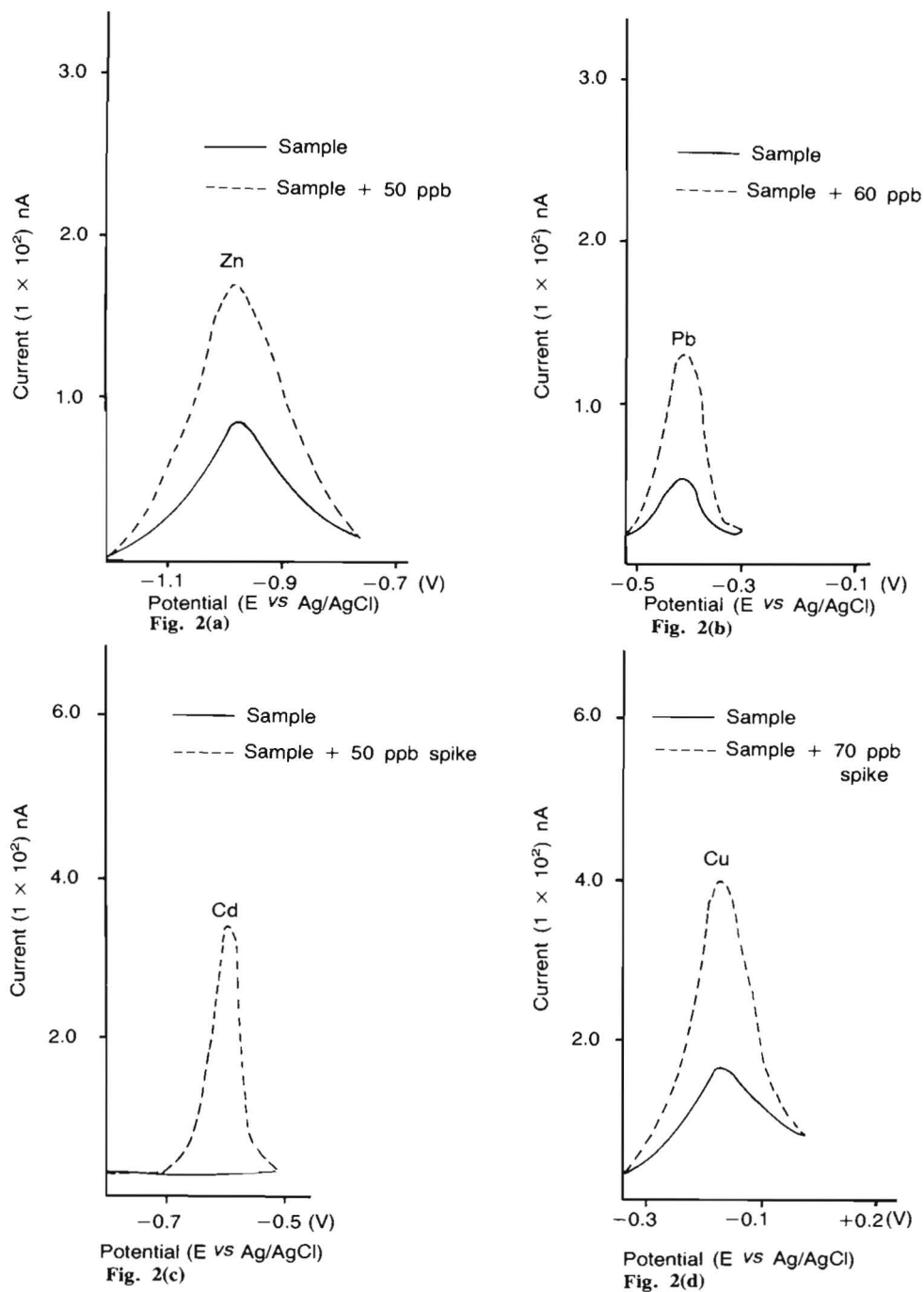
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Fig. 2. Typical anodic stripping voltammograms for 2(a) Zn, 2(b) Pb, 2(c) Cd and 2(d) Cu, using various tap water samples.

Table 2. Results of Analysis of Trace Metals in Tap Water Using (DPASV)

Element	Mean conc. found (ppb)	S.D.[*] (±)	R.S.D.[*] %	Maximum permissible level in drinking water (15) ppb
Pb	33.3	2.5	7.5	100
Cd	–	–	–	10
Cu	29.1	2.3	8.0	1.5×10^3
Zn	124.6	8.3	6.7	1.5×10^4

(*) Nine replicate measurements were performed.

S.D. ≡ Standard deviation.

R.S.D. ≡ Relative standard deviation.

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تحديد العناصر الزهيدة في مياه الصنبور من الرصاص والكادميوم والنحاس والخارصين بطريقة الخلع المصعدي الجهدي

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قسم الكيمياء الصيدلية ـ كلية الصيدلة ـ جامعة الملك سعود ـ ص . ب ٢٤٥٧ الرياض ١١٤٥١
المملكة العربية السعودية

يقدم هذا البحث النتائج العملية لتحديد عناصر الرصاص، الكادميوم،
النحاس والخارصين الموجودة في مستويات منخفضة جداً «جزء في البليون» في
مياه صنبور المختبر باستخدام الخلع المصعدي الجهدي ورصد النتائج بطريقة
النبض التفاضلي الحساسة في محلول ثلاثي سترات النشادر الداعم. وتمت
قياسات التجارب بطريقة الإضافة القياسية حيث سجلت المنحنيات الجهدية
التفاضلية النبضية المصعدية للعينات قبل وبعد الإضافة القياسية في مدى الجهد
صفر إلى – ١,٢ فولت. واستعمل جهاز محلل بولاروغرافي يشتمل على حاسب
آلي صغير. وتتكون أقطاب الخلية من القطب الكاشف وهو عبارة عن نقطة
ساكنة من الزئبق وقطب مرجعي من الفضة وكلوريد الفضة في محلول كلوريد
البوتاسيوم المشبع وقطب البلاتين المساند.

وكانت الاختلافات في النتائج، بطريقة الإضافة القياسية للعناصر، أقل
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