Single-sweep polarography offers many advantages to the chemist who is faced with the control and analysis of water quality today. Some of these such as a technique that can characterize soluble species; a highly sensitive (parts-per-billion) method suitable for field operation, automation, and continuous monitoring; and direct analyses, with preconcentration or separation of the micropollutant from the water sample many times unnecessary, and matrix problems of interference minimized, are discussed. Single-sweep polarographic procedures have been developed in these laboratories that have proved useful in detecting and analyzing for a number of micropollutants of river water, well and spring water, tap water, sea water, and effluent waters from many sources. Potential methods of analysis are discussed for chromium (Cr<sup>III</sup> and Cr<sup>VI</sup>), arsenic (As<sup>III</sup> and As<sup>V</sup>), and iodine (I<sup>-</sup> and IO<sub>3</sub><sup>-</sup>) soluble ionic species. Some uranium, selenium, lead, cadmium, tellurium, thallium, manganese, copper, nickel, and zinc ionic species were also studied and techniques are presented for their analysis. Techniques for the single-sweep polarographic analysis of traces of explosives and plasticizers in water, such as nitroglycerine, 1,2-propylene glycol dinitrate, 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitro-1,3,5-hexahydrotriazine (RDX), diethyl phthalate, and dibutyl sebacate are also presented and discussed.

Single-sweep polarography (1) is a simple, rapid, and inexpensive method of trace element analysis that offers many advantages in the surveillance and control of micropollutants that may find their way into our ground and surface water supplies.

It is the purpose of this research to present and describe some useful single-sweep polarographic techniques that have been developed and used in this laboratory (2, 3) for detecting and measuring directly extremely low levels of cationic and anionic species as well as some organic micropollutants in natural water. These techniques require little or no prior concentration of the pollutant and only a few milliliters of sample is needed for the analysis.

**EXPERIMENTAL**

In general, ground water is purer than surface water due to the fact that it is more remote both physically and in time from environmental pollution. Since the drinking and domestic water supply of this Center (NWC) is obtained from fairly deep and uncontaminated wells (200 to 800 feet), it was decided to use this water as a standard to establish a norm or baseline from which toxic micro pollutants might be rapidly detected and measured if they entered the water supply. This water provided a large supply of a relatively low level metal soluble species and low level organic material supporting electrolyte for the polarographic studies. The well water used is very low in organic ligands which are potentially strong complexing agents and interfere seriously in some trace element analysis. This was determined by standard additions of both Cu<sup>2+</sup> and Zn<sup>2+</sup> to the well water. The single-sweep polarograms for both Cu<sup>2+</sup> and Zn<sup>2+</sup> proved to be linear in the part-per-billion concentration range, thus indicating the amount of complexing agents present in the water to be noninterfering. If the water does contain interfering organic matter, then it must be removed before analyzing for the ions that are discussed in this study.

**Apparatus and Materials.** A single-sweep polarograph, known as the A-1660 Davis Differential Cathode-Ray Polarotrace, manufactured by Southern Analytical Instruments Company, England, was used in this work. A Moseley 2D X-Y recorder was used to record the polarographic data.

The polarographic measurements were made at 25°C ± 0.1°C on 2 milliliters of water placed in a 5-millilitre capacity quartz cell. 

The dropping mercury electrodes were used in this work had drop times of 7 seconds in distilled water and m = 5 to 7 milligrams per drop. Dissolved oxygen was removed from all solutions prior to recording the polarograms with oxygen-free nitrogen obtained by passing nitrogen gas over copper metal turnings at 450°C. Redistilled mercury was used as the anode and all current peak potential values are referred to the mercury pool.

Standard solutions of inorganic ions used in these studies were made from water of high purity (0.42 × 10<sup>-6</sup> mho cm<sup>-1</sup>) at 25°C and were obtained by diluting primary standard solutions (1.0 ppm per milliliter) to the desired concentration. Oxi-Analytical Chemicals, Austin, Texas. Chemicals used as supporting electrolytes or chemical reaction agents were reagent grade and, if needed, further purified by electrolysis over a mercury pool. Since only drops or microliters of these solutions were added to the water studied, these solutions were sufficiently free of the particular trace element sought for precise analysis at the part-per-billion level. All organic compounds used in these studies were 95-99% pure.

The well water used in this investigation was sampled from sites where repeated sampling over a twenty-year period to detect major water-quality changes and stability has been made. Good well schedules and other information such as domestic water analysis data pertinent to pollution studies were available. The underground water in this desert area is associated with heterogeneous rock formations, highly mineralized, and resembles a dilute brine in chemical composition. The dissolved solids content in the water from the wells used in this study is near or slightly below the 500 mg per liter recommended limit by the U.S. Public Health Service and the chemical quality is good. It proved to be an excellent supporting electrolyte for these studies.

All water samples were collected in pint- and quart-size polyethylene containers that had been carefully washed with 6N Reagent hydrochloric acid. The containers were then rinsed several times with distilled water and finally with the respective water before filling the container for analysis. As little time as possible between collection of the sample and the trace element analysis was adhered to throughout this work (24 to 72 hours in most cases) to minimize either loss of the trace element to the polyethylene or gain of the trace element through leaching action of the water on the polyethylene.

The trace elements and organic substances studied in this work were found to give well-defined single-sweep polarograms that are proportional to concentration over a range of 5 × 10<sup>-10</sup> to 5 × 10<sup>-9</sup> gram per milliliter in most solutions studied.

**Procedures.** 1) A 2-ml aliquot of the ground or surface water is placed in a 5-ml capacity quartz cell, to which a small volume of CP mercury has been added as the anode; the dropping mercury electrode is then inserted into the solution in the cell and the sample is flushed with oxygen-free nitrogen for 3-5 minutes to remove the dissolved oxygen from the water. The sample is examined for the presence of both cationic and anionic micropollutants by first setting the start potential of the polarograph at -0.05 volt and recording the current-voltage curve. The start potential is then set to -0.50 volt and the current-voltage curve is again recorded. Measurements of -0.45-volt increments are made in this manner through the range of -0.05 to -1.90 volts. A number of species can sometimes be identified and determined on a single aliquot of the original water. For example, Cu<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup>, IO<sub>3</sub> -, and Mn<sup>2+</sup>...
can all be determined in the same aliquot of water by changing the start potential of the polarograph as described above to record the polarograms for each element and by the method of standard addition identify and determine the concentration of each. In typical well water, a Cu^{2+} polarogram will appear near -0.25 V, Cd^{2+} near -0.70 V, Zn^{2+} near -1.15 V, IO_3^- near -1.23 V, and Mn^{2+} near -1.60 V. The Zn^{2+} and IO_3^- polarograms may overlap if both species are present. If one observes a double wave in this voltage region, the sample is made 0.1M in EDTA to complex the Zn^{2+} and allow one to measure the IO_3^- alone. The Zn^{2+} can be measured alone by reducing the IO_3^- to I^- with a mild reducing agent since the I^- does not give a polarogram in the region of Zn^{2+}.

The micropollutant can then be identified by adding micro- aliquots of the suspected ion to the water in the polarographic cell. The wave should increase in height at precisely the peak potential seen in the original sample if the pollutant is that ion. The concentration of each ion that produces a measurable polarogram in the water sample is then obtained by adding a micro- aliquot of a standard solution of that respective ion to the 2-mI aliquot of water in the cell and recording a second single-sweep polarogram. The concentration of the respective ion can then be obtained from a ratio of the two polarogram wave-heights. For best results, one should add just enough known ion to raise the wave height about twice the original height.

2) After the concentration for some trace element species has been established by the above procedure in the original untreated natural water as received, micro-additions of polarographic grade reagents (directly to the water) such as HCl, H_2SO_4, NaOH, chlorine water, KCNS-acetic acid, HClO_4-pyrogallol, HCl-tartaric acid, and NH_4OH-NH_4Cl, can then help establish base-line concentrations in these respective media for reference in quickly detecting these species and other species of micropollutants if they enter the water supply. The concentrations of these reagents added can vary from concentrated HCl and H_2SO_4 to 0.2M solutions of others. Examples of this technique are shown in Figures 1, 2, and 3 with iodine, uranium, and selenium, respectively, in sea water and well water. Iodine, as I_2, produces a well-defined polarogram in natural water around -1.2 volts vs. a Hg pool. Iodine, as I^- does not interfere. The iodide (I^-) concentration can then be determined by converting the I^- to IO_3^- with chlorine water and again measuring the IO_3^- wave. Ions that may interfere, such as Zn^{2+} which sometimes overlaps with the IO_3^- wave, can be complexed with EDTA or some other suitable chelating agent in the media before recording the wave for IO_3^-.

Figure 1. Iodide and iodate in sea water

Figure 2. Uranium(VI) in sea water, 0.05M in tartaric acid and 0.05M in triethanolamine

Figure 3. Selenium(VI) in well water, 0.05M in HCl and 0.05M in tartaric acid (3.4 x 10^-7 g/ml)

Figure 4. Chromium in well water; Cr^{6+} (-0.60 V) in 0.25MKCNS and 0.01N NaOH, Cr^{3+} (-1.25 V) in 1N NaOH

The solid line (Curve C) represents the increase in the IO_3^- wave height due to the oxidation of I^- present in the sample to IO_3^- upon the addition of chlorine water (2 drops of a 5% solution) to a 2-mI water sample. The upper curve represents the standard addition of a known concentration of IO_3^- to the original sample (bottom curve). Uranium gives two well-defined peaks at -0.58 V and -0.72 V, respectively, in 0.05M tartaric acid-0.05M tartaric acid (Figure 2), while selenium gives well-defined peaks at -0.71 V and 1.18 V, respectively, in HCl-tartaric acid (top two curves (Figure 3). Thus, by using different supporting electrolytes one can soon look for the presence of a pollutant, characterize the species, and by the standard addition technique determine its concentration directly in the sample. A change in the start potential used in single-sweep polarography may also be helpful in characterizing a species, as can be seen in the double peak shown for selenium(IV) (bottom curve, Figure 3). Cu^{2+}, Pb^{2+}, Cd^{2+}, Sn^{2+}, Sn^{4+}, As^{3+}, As^{5+}, Sb^{3+}, Sn^{4+}, and Bi^{3+} are examples of species that can be found in HCl or H_2SO_4 (0.1 to 1N). Zn^{2+} gives well-defined polarograms in 0.5M KCNS and NH_4OH-NH_4Cl (1M each), respectively, while Cr^{3+} gives a good wave for measurement in 0.25M KCNS-0.01N HAc (pH 3.2). Some very useful tables of half-wave potentials of the reduction of both inorganic species and organic substances in different supporting electrolytes can be found in Chapter XIII of Ref. (4) in this study.

3) Some other techniques that have proved to be useful to establish the speciation of a pollutant in natural water are described as follows: (a) Chromium, as either Cr^{3+} or Cr^{6+} can be determined. The Cr^{3+} species gives a well-defined single-sweep polarogram in the presence of KCNS and acetic acid, while the Cr^{6+} species does not. The Cr^{3+} species can then be determined in a NaOH media, where it gives a well-defined polarogram and the Cr^{3+} species does not interfere. Figure 4 shows typical data for chromium in well water. (b) Arsenic can be determined as either As^{3+} or As^{5+}. As^{3+} gives a well-defined polarogram in H_2SO_4 solution while As^{5+} is inactive (non-electroactive species). As^{3+} and As^{5+} both give well-defined single-sweep polarograms in a HClO_4-pyrogallol media. Figure 5 shows typical data for arsenic.

RESULTS AND DISCUSSION

Table I shows the concentration of some soluble free inorganic species of trace elements found in the well water at NWC by the single-sweep polarographic techniques de-
scribed in this study. The data were obtained without prior concentration of the species and by the addition of purified reagents to the original water sample only where necessary to obtain the best polarogram for quantitative results. For example, the IO$^{-3}$ concentration was obtained from the original sample with no addition of any reagent. The Au$^{3+}$ data were obtained in a 1 M NaOH media and the NO$^{-3}$ data (5) in the presence of uranyl ion in acidic media. Cu$^{2+}$, Mn$^{2+}$, and Zn$^{2+}$ were determined (as the free ionic specie) in the original water as received with no reagents added. As$^{5+}$ was determined in H$_2$SO$_4$ media (6) by the addition of As$^{5+}$ free H$_2$SO$_4$ to the original water sample (3 drops concentrated H$_2$SO$_4$ for 2 milliliters of sample). The data in Table I represent only the free ionic species in solution; they do not represent, in most water samples, a total elemental concentration such as atomic absorption spectrometry or neutron activation methods of analysis would give.

A previous contribution by Offner and Witucki (7) showed that antimony, arsenic, cadmium, lead, mercury, selenium, tellurium, and thallium could all be rapidly detected and measured as a group in water at their acute toxic levels by classical polarography using a dropping mercury electrode with the Sargent Model XXI polarograph. However, the time required to obtain the complete polarogram with this instrument is about 5 to 10 minutes and the lower limit of detection is around 5 ppm. With the same procedure and a single-sweep polarograph of the type described herein, all these toxic elements, with the exception of mercury, should be readily detected and measured to levels as low as 5 parts-per-billion (5 ppb). The time required for analysis is considerably less with single-sweep polarography, and if a toxic group analysis is made where the total current is measured at a constant applied potential of around -0.8 volt, the data can be recorded continuously every 7 seconds in the tartaric-hydrochloric acid supporting electrolyte recommended in Offner's work. The method should be amenable to an automated and continuous polarographic analysis for these toxic elements in natural waters.

The procedures described in this work are very useful in determining whether a sample of natural water is contaminated with toxic trace substances. If a base or norm has been previously obtained on the same water, the data can quickly provide information on subtle changes and contamination of the water. The base or norm is established by the use of several supporting electrolytes to establish proof and concentration of the various soluble species that are present. Thus, the water is examined first directly as it comes from the source (well, tap, river, stream, etc.) with single-sweep polarography and then in the acidic, basic, and complexing media, respectively, that have been discussed in this work. From these polarographic data, one can then identify and measure the concentration of many cationic species such as arsenic, lead, cadmium, copper, nickel, cobalt, iodine, selenium, chromium, aluminum, manganese, tellurium, thallium, iron, antimony, tin, uranium, etc., as well as anionic species such as nitrate, nitrite, cyanide, sulfite, sulfide, chromate, fluoride, iodide, iodate, molybdate, and vanadate if they are present originally or if they enter the water supply. Maienthal and Taylor (8) have used single-sweep polarography to determine many of the above species in natural water. This is an excellent reference to some reliable field tested procedures related to those described in this study. K. H. Mancy (9, 10) and P. Nangniot (11), respectively, provide other good references.

In addition to inorganic contaminants of natural water, the single-sweep polarographic method of analysis provides a quick screening method to identify and determine many organic pollutants if they find their way into the water supply (12, 13). Typical data for explosives such as nitroglycerine, TNT, RDX, 1,2-propylene glycol dinitrate, and 2,4-dinitrotoluene in natural water are shown in Figures 6, 7, and 8. Plasticizers, such as diethyl phthalate and dibutyl sebacate can be identified and measured in admixture if they enter the water supply (14). Typical data are shown in Figure 9. Formaldehyde, acetaldehyde, acetone, nitrobenzene, arsenic derivatives such as lewisite, DDT, and many other organic environmental pollutants are amenable to polarographic techniques. Since these techniques are sensitive to parts-per-billion, a great number of organic sub-

![Figure 5. Arsenic in well water, 0.5 N in HClO$_4$ and 0.1 N in pyrogalol (0.625 ppm)](image)

![Figure 6. RDX in lake water, 0.10 mM](image)

![Figure 7. 1,2-Propylene glycol dinitrate in sea water](image)
stances are water-soluble enough to be directly measured by polarography as a contaminant of a water supply. The same procedures described for determining inorganic species directly in a natural water are used and the organic material is also determined by the standard addition method. Extractions of the organic substances from the water with organic solvents are generally necessary to establish positive identity; however, if the organic substance is present in an amount over that normally found for an inorganic substance that might interfere in a particular normalized water supply (where one knows the inorganic trace elements present), it may be possible to determine it directly without extraction. For example, Figure 10 shows the presence of RDX as a pollutant in a sample of well water without prior extraction being necessary for the analysis. Separation and concentration of an organic pollutant from the water can be accomplished by extracting the material with small volumes of solvents such as benzene, n-hexane, chloroform, etc., evaporating the solvents, and then determining the pollutant by polarography in the usual manner with a suitable supporting electrolyte. For example, 2 milliliters of pure benzene can be added to a 500-milliliter sample of natural water to extract an explosive such as RDX from the water. The 2 ml of benzene is then evaporated and the RDX is taken up in a supporting electrolyte of 0.1M LiCl in 75% acetone for the single-sweep polarographic analysis. Recently an excellent reference by J. S. Hetman on the polarography of explosives (15) appeared in the literature. This paper presents a summary of polarographic techniques useful in determining many types of explosives.

CONCLUSION

Single-sweep polarography offers a unique capability among modern trace element methods of analysis in its ability to analyze directly and continuously for a large number of species of both inorganic and organic micropol- lutants in ground and surface waters. Concentration methods that are time consuming and introduce contamination problems can be kept to a minimum. The main advantages of the single-sweep polarographic procedures presented in this manuscript and those developed and tried by the author appear to be the following:

1) Rapid, simple, and inexpensive techniques that can characterize and analyze chemical species directly in water.
2) Milliliter samples that provide part-per-billion sensitivity.
3) Methods suited to direct and continuous analysis in the field with automation capability.
4) Standard addition procedures that minimize matrix interference problems.

5) Multi-element analyses many times possible on a single aliquot of water.
6) Preconcentration or separation of pollutant from water many times unnecessary.
7) A large number of organic and inorganic pollutants are amenable to the techniques.

The potentials of the procedures described and techniques presented in this work are many and await only the application by the person faced with the complex analytical problems in water pollution studies today.

LITERATURE CITED