AL/EQ-TR-1995-0004

DETERMINATION OF THE OXIDATIVE REDOX CAPACITY OF AQUIFER SEDIMENT MATERIAL BY SPECTROCHEMICAL COULOMETRIC TITRATION

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February 1996

Final Technical Report for Period June 1994 - August 1994

AIR FORCE MATERIEL COMMAND
TYNDALL AIR FORCE BASE, FLORIDA 32403-5323

ARMSTRONG LABORATORY

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	February 1996	Final JUN 94 - AUG 94

4. TITLE AND SUBTITLE
Determination of the Oxidative Redox Capacity of Aquifer Sediment Material By Spectrochemical Coulometric Titration

5. FUNDING NUMBERS
F49620-93-C-0063

6. AUTHOR(S)
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
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8. PERFORMING ORGANIZATION REPORT NUMBER
N/A

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
ARMSTRONG LAB/EQC
139 Barnes Drive
Tyndall AFB, FL 32403-6001

10. SPONSORING / MONITORING AGENCY REPORT NUMBER
AL/EQ-TR-1995-0004

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT
UNLIMITED DISTRIBUTION

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Methodology was developed for determination of the oxidative redox capacity of aquifer sediment material by the method of spectroelectrochemical coulometric titration. This method involves the measurement of absorbance of sediment particles slurries at the maximum absorption wavelengths of the optically detectable mediator-titrant (reporter) molecules resorufin and methyl viologen as a function of the charge passed in a constant-potential coulometric titration. Titration was carried out on diluted, dry-sieved Columbus Air Force Base material of particle size smaller than 75μm diameter. Resorufin was reduced first, followed by methyl viologen. There was no perceptible delay between completion of titration of resorufin and the initiation of titration of methyl viologen. Based on the uncertainties of measurement, it could be estimated that the upper limit of oxidative redox capacity of the Columbus aquifer material was ca. 3 microequivalents per gram of solid material. More precise determination of oxidative redox capacity will require use of methods such as fluorescence which are more immune to the effects of scattered light than absorption spectrophotometry, and will allow higher loading of suspended solids than the current absorbance based method.

14. SUBJECT TERMS
REDOX, SPECTROCHEMICAL, OXIDATION CAPACITY

15. NUMBER OF PAGES
20

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
U	U	U	UL

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PREFACE

This report was originally prepared for RDL under Contract number F49620-93-C-0063 for the Air Force Office of Scientific Research, Bolling Air Force Base, Washington D.C. It contains results of summer faculty research sponsored by the Armstrong Laboratory Environics Directorate, Tyndall Air Force Base, Florida 32403-5323.

This report covers research performed by Dr. James L. Anderson and Mark C. Delgado of the University of Georgia between June and August 1994. The report is being reprinted and submitted to Defense Technical Information Center because of its widespread interest to the DOD regarding the fate and transport of hazardous wastes. The AL/EQC Mentor was Dr. Thomas B. Stauffer. Mary Reynolds was the AL/EQ Summer Faculty Coordinator.

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Final Report for:
Summer Faculty Research Program
and
Graduate Student Research Program
Armstrong Laboratory, Environics Division
AL/EQC
Tyndall Air Force Base, Panama City, FL

Sponsored by:

Air Force Office of Scientific Research
Bolling Air Force Base, Washington, D. C.
and
Armstrong Laboratory

September, 1994

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Abstract

Methodology was developed for determination of the oxidative redox capacity of aquifer sediment material by the method of spectroelectrochemical coulometric titration. This method involves the measurement of absorbance of sediment particle slurries at the maximum absorption wavelengths of the optically detectable mediator-titrant (reporter) molecules resorufin and methyl viologen as a function of the charge passed in a constant-potential coulometric titration. An approach which was successful for determination of the oxidative redox capacity of a pond sediment rich in organic matter and iron species was extended to an oxidized aquifer sediment material of low organic carbon and iron species content sampled from Columbus Air Force Base, Mississippi. Titration was carried out on diluted, dry-sieved material of particle size smaller than 75 μm diameter, suspended in aqueous, pH 7, 0.1 ionic strength phosphate buffer at 0.0426 % sediment by weight. Blank titration was carried out on a sample of identical composition but in absence of the aquifer material. In both cases, resorufin was reduced first, followed by methyl viologen. There was no perceptible delay between completion of titration of resorufin and the initiation of titration of methyl viologen. This behavior contrasted significantly with the titration of pond sediment of high organic and iron species content, which showed a very significant break between completion of titration of resorufin and initiation of titration of methyl viologen. Based on the uncertainties of measurement, it could be estimated that the upper limit of oxidative redox capacity of the Columbus aquifer material was ca. 3 microequivalents per gram of solid material. This estimate is in the vicinity of the values of redox capacity of aquifer material obtained from other sites by one other research group, but not consistent with the values reported by another group. More precise determination of oxidative redox capacity will require use of methods such as fluorescence which are more immune to the effects of scattered light than absorption spectrophotometry, and will allow higher loading of suspended solids than the current absorbance-based method. Additional studies identified the importance of thermal expansion of aqueous solutions as a cause of oxygen leakage into closed vessels when temperature is not regulated, and demonstrated that huge pressure changes (900 psi over a range of 22 °C) can occur when the temperature of an aqueous sample is allowed to vary by small amounts. Methods were devised to overcome this problem by the combination of a thermoisolation chamber to control the temperature of the sample and exclude oxygen from the titration zone.

DETERMINATION OF THE OXIDATIVE REDOX CAPACITY OF AQUIFER SEDIMENT MATERIAL BY SPECTROELECTROCHEMICAL COULOMETRIC TITRATION

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Introduction

The remediation of many polluted sites, whether by in situ processes such as chemical or biological natural attenuation or by processes involving the addition of externally supplied chemical or biological agents, frequently involves redox processes. The feasibility and total transformation capacity of such processes is ultimately limited by the redox capacity of the environmental system to be transformed. In this context, redox capacity is a measure of the number of molar equivalents of electrons which can be donated (reductive redox capacity) or taken up (oxidative redox capacity) by the system in the course of a redox transformation of an externally added agent such as a pollutant. The redox capacity limits the ultimate quantity of pollutant which can be oxidatively or reductively transformed by the system, since for each mole of pollutant oxidatively or reductively transformed, a stoichiometrically related number of moles of oxidant or reductant in the environment must also be transformed. Once all electron donors or acceptors initially available in the system to drive the transformation of interest have been exhausted, the transformation must stop. In addition, the redox capacity is an important quantity in assessing the feasibility of driving a transformation process by the addition of an external chemical or biological agent, by providing an estimate of the quantity of external agent required either to supplement or to oppose the natural capacity of the system in driving a desired transformation.

Unfortunately, the present knowledge of redox capacity of natural systems is limited. Only a relatively small number of studies has been carried out to assess this important information (1-3) in sediments. Data from two of these studies on apparently very similar aquifer sedimentary materials are in significant conflict regarding the magnitude of the oxidative redox capacity of the sediments (1,2). The methodologies of these two studies are based on classical chemical titrations with very reactive chemical reductants, requiring rather long

equilibration times, rigorous oxygen exclusion over long periods, and centrifugation and filtration to overcome interference with spectrophotometric measurements due to light scattering by sediment particles.

We have developed an alternative indirect spectroelectrochemical coulometric titration approach in which the optical signal of an added indicator reagent is used together with coulometry to assess the number of oxidative equivalents of sediment components present. Reagents are generated in situ in the titration vessel as needed, thereby avoiding some of the problems in earlier work of storing very reactive, potentially unstable reagents for long periods of time. The approach also enables measurements in the presence of suspensions of sediment particles, without need for particle removal prior to spectrophotometric measurements. The indicator reagent provides the spectral signal, so that the approach is applicable even to samples that contain no chromophore. Our earlier work on redox capacity of a pond sediment (3,4) yielded results which were compatible with the results of Barcelona and Holm for aquifer material (1), but significantly higher than the results of Heron et al. for aquifer material (2).

In this investigation, we examine the use and limitations of the spectroelectrochemical methodology to probe the redox capacity of aquifer material more directly comparable to the material investigated by Barcelona and Holm (1) and Heron et al. (2). In addition, in the process of investigating the possible sources of an oxygen leak during the development of this methodology, we have discovered the enormous pressure changes (as great as 900 psi for a temperature change of 22 °C) that can be generated by thermal expansion of aqueous solutions in a closed vessel when temperature is allowed to vary. Methods were developed to overcome this practical problem in titration cells. A model for the dependence of pressure change on temperature was developed and compared with experiment. The enormous pressure change observed can be quite well explained based on the known thermal expansion coefficients and compressibility of water and their temperature dependence.

Methodology

Spectroelectrochemical methods have been previously used to coulometrically titrate biological components(5,6). A tin oxide working electrode is used to transfer electrons to or accept electrons from electrogenerated titrants which in turn transfer charge to or from the

biological species of interest. The working electrode may be used to drive either oxidative or reductive processes, by controlling the applied potential in an appropriate region. This approach is well-suited for reliable quantitation of low micromolar concentrations of spectrally visible and invisible species (7). Major advantages of the approach include the ability to work in a closed system of small volume, with oxygen removal before and exclusion during the titration; with accurate and quantitative addition of titrant at a controlled rate; and the feasibility of carrying out both forward and back titration of the component of interest to assess the reversibility of the process in a single titration experiment if desired (5).

In a conventional chemical titration, reagents must be added to the system from external reservoirs, thus continually changing the total mass, composition, and volume of the system. The spectroelectrochemical titration method described here does not suffer this problem, since the reagents are electrons generated or consumed by reactions at the working electrode in a closed system. Thus, the titrant species can be introduced into the system in a stable form which will not react with the species under study until the titration is initiated by applying an appropriate potential to the working electrode. Quantitation can be achieved electrically, by counting electrons (measured by the charge passed during the titration). In the experiments described here, the sample of interest was mixed with the reagents in inactive form, deoxygenated, and transferred into an electrochemical cell designed to isolate the solution from the ambient atmosphere. A detailed description of the cell and the degassing procedure follows.

Cell Design and Degassing Procedure

A diagram of the electrochemical cell and the electrodes appears in Figure 1. The cell consists of a main chamber constructed of 1 cm i.d. square Pyrex stock to which two sidearms and a valve with an inlet ground glass fitting have been attached. The valve allows introduction and isolation of samples from the ambient atmosphere. Samples are degassed in a degassing bulb connected to the valve via the ground glass fitting.

An inner Luer ground glass fitting was used for initial experiments, but was replaced with a 10/30 standard taper inner fitting due to significant problems in assuring that the joint did not leak and inadvertently admit oxygen to the solution. The two sidearms are fitted with an outer ground glass fitting (7/15). Each sidearm is joined to the main chamber through a medium

porosity frit. The reference and auxiliary electrode chambers are both made of Pyrex glass which terminate in 7/15 standard taper inner ground-glass fittings. The reference and auxiliary chambers are filled with 1.0 M KCl solution, and a Ag wire anodized in 6 M HCl to form a AgCl coating is inserted through a septum cap at the top of each electrode compartment to make the Ag/AgCl electrode.

Two chamber designs were used. The initial design had a single piece body, terminated with a porous Vycor frit epoxied into a 5 mm diameter glass tube extending from the lower end of the 7/15 fitting for contact with the cell solution. A serious problem with this design was the inability to maintain reproducibly any gas expansion volume when the cell was filled by vacuum degassing. This design was susceptible to leakage due to temperature elevation in the spectrometer sample compartment during an experiment, causing significant pressure increases due to water expansion. One or more 7/15 joints would open to relieve the otherwise disastrous pressure rise in the cell, giving rise to concomitant oxygen leakage into the cell. The revised electrode chamber was designed to allow retention of a gas space for liquid expansion, to prevent large pressure buildups due to thermal expansion of water in a system without such an expansion space.

In place of the septum cap, a 5 mm diameter Kontes Bevel-Seal threaded O-ring connector was sealed to the top of the 7/15 joint. A 3 mm diameter glass tube served as the reference or auxiliary electrode compartment. A piece of 3 mm porous Vycor rod was epoxied into a short length of 5 mm diameter tubing fused to the lower end of this 3 mm diameter tube. The tube passed through an O-ring placed above the 5 mm diameter section, through the 7/15 joint, and finally through the Bevel-Seal O-ring joint. The reference or auxiliary Ag/AgCl electrode protruded from the end of the tube, which was capped with an inverted septum cap. Because the tube passed through two O-rings, the electrode compartment could be slid up and down in the chamber. While the cell was being degassed prior to filling, the electrode compartment tube was slid down into the sidearm to attempt to make the gas volume above the lower O-ring accessible for oxygen removal and replacement by helium. When the cell was to be filled, the electrode compartment tube was pulled up so that the expanded lower end held the O-ring against the bottom of the inner 7/15 joint to preserve a gas space above the O-ring into which thermally expanding liquid could flow in the event of inadequate thermal control. This

approach should thus cut down on oxygen leakage. In fact the rate of oxygen leakage during titrations decreased more than an order of magnitude when the above sidearm design was used in conjunction with a thermostated chamber filled with helium to exclude oxygen from the atmosphere surrounding the cell during a titration. However, exclusion of oxygen was not consistently successful during the sample degassing process.

A section of 26 gauge platinum wire was flame-sealed into the cell to serve as a potentiometric electrode. The working electrode for the reduction steps was a 2.5 cm square piece of SnO_2 glass epoxied to the bottom of the main chamber of the cell with Devcon 2-Ton clear epoxy. The square edges of the working electrode were also used to align the cell in a square positioning recess in the optical train of the spectrophotometer. The main chamber of the cell held 1.85 mL of solution, which could be circulated by a magnetic stirrer. The stir bar was constructed by flame-sealing a ca. 7 mm long piece of steel paper clip inside Pyrex glass under vacuum. The stirrer was driven by a water-propelled magnetic impeller supplied with thermostated water from a circulating temperature regulator bath. The water was also circulated in the walls of an isolation chamber whose function was both to control the cell temperature and to bathe the cell in a nitrogen atmosphere to exclude oxygen access during the titration. Light was passed through the main chamber of the cell to determine the absorbance. Because the cell was made from Pyrex glass, light was detected primarily in the visible region of the spectrum.

Solutions to be studied were degassed and introduced into the cell under an inert atmosphere. The degassing assembly consisted of a Ridox catalyst, a helium inert gas line, a water-filled bubbler to saturate the inert gas with water, and a vacuum line with a liquid nitrogen trap and a Drierite drying column to prevent water from entering the mechanical vacuum pump. The helium was passed through a dryer and a Restek oxygen scrubber catalyst before it entered the Ridox catalyst chamber. The electrochemical cell could be either pressurized with the inert gas or evacuated via a two-way valve on the degassing assembly. All pieces of the degassing assembly were joined by ground glass fittings greased with Apiezon L or Apiezon N. The vacuum pump and the Drierite column were connected to the all-glass degassing apparatus by butyl rubber tubing.

The two-way valve was set to evacuate the solution degassing bulb/cell adapter and the cell for at least 15 min. prior to filling. The cell was then alternately evacuated for at least 1

min., followed by ca. 30 seconds of helium sparging, for a minimum of four cycles. The cell stopcock was closed off and the cell was removed from the degassing assembly. Both the reference and auxiliary electrodes chambers were degassed via a needle inserted through the septum cap while attached to the cell. They were evacuated and filled with an inert gas alternately for 2 min. for 5 cycles. After the electrodes had been degassed, they were evacuated and immediately filled by means of a 1 mL syringe with a previously degassed 1.0M KCl solution. If a bubble which might interfere with the solution conductivity appeared in a sidearm electrode compartment, the compartment was reevacuated and the degassing process was repeated for that electrode.

Once the reference and auxiliary electrode chambers were filled, the solution to be studied was introduced into the degassing bulb. At this point, both the bulb and the cell were reattached to the degassing assembly. The solution was then degassed by alternately exposing it to the inert gas and vacuum while it was being stirred. The solution was then introduced into the cell by opening the valves between the cell and the degassing bulb and simultaneously pulling vacuum in the cell and the degassing assembly. The cell and degassing bulb were tilted downward and the cell was filled by pressurizing the degassing bulb with the inert gas. To minimize bubble formation, vacuum was applied briefly and inert gas was again introduced into the degassing bulb. This procedure was repeated until no large bubbles were visible inside the cell.

Apparatus

The potentiostat which was used to control the experiment was custom-built for the purpose. Current output was converted to voltage by a current-to-voltage converter, and fed to a custom-built absolute value circuit which converted all signals to a positive value for input into a voltage-to-frequency converter (Datel) with a calibration factor of 10 kHz per volt at the input. The train of pulses from the voltage-to-frequency converter was fed to a counter-timer (Data Precision 5740) in the count mode. With a current output gain of 100 microamperes per volt, the counter had an output of 100,000 counts per millicoulomb of charge passed, with an accuracy better than 0.1 %.

The spectrophotometer was a Perkin-Elmer Model 3840 diode array spectrometer.

controlled by a Perkin-Elmer 7500 computer. All spectral scans were obtained in the survey mode, which had an excessive level of stray light (specified as 3 %, and measured to be ca. 2.5 %), due to mechanical problems which prevented operation in the high resolution mode, which had dramatically better stray light specifications. Spectra were recorded and stored on floppy diskettes. In some cases, data were converted to ASCII files and copied to a Sun Sparcstation computer for further processing.

A thermostated housing and platform were custom fabricated to adapt the nonstandard dimensions of the electrochemical cell to the spectrophotometer sample compartment. The thermostated housing was constructed from two 1/2 inch thick aluminum plates, through which water from a temperature bath was circulated, and poly(methylmethacrylate) to enable visual observation of the cell assembly. The housing was lowered over the cell and clamped to the platform. Nitrogen was circulated through the interior of the thermostated chamber to exclude oxygen from access to the exterior of the cell. Oil bubblers placed in the supply line to the thermostated chamber and in the outlet line from the chamber were used to visualize the flow of nitrogen into the system.

Pressure measurement equipment

Experiments were carried out to determine the dependence of pressure in a closed vessel on the temperature of the vessel. The vessel consisted of 1/4 inch diameter stainless steel tubing of ca. 1.25 mL internal volume, with a Helicoid 0-5000 pounds per square inch (psi) liquid chromatographic pressure gauge in a tee configuration, and two high pressure valves at either end. With the inlet valve closed and the outlet valve open, the system was evacuated. After closing the outlet valve, the inlet valve was opened and the system was pressurized to 1000 psi at 25 °C by pumping water in from an Altex Model 110A HPLC pump, and the inlet valve was closed. The vessel was equilibrated in a controlled temperature water bath overnight, to insure that there were no leaks. The temperature was then varied in random order over the range between 13 °C and 35 °C, in approximately 2 °C increments according to a sequence selected by use of a random number generator. Triplicate readings were obtained after the temperature had reached a stable, constant value. The final measurement was made at the initial temperature to check for any long-term leakage, which was found to be negligible. Temperatures were

measured with the temperature probe of a Yellow Springs Instrument YSI Model 33 conductivity meter and with a Radio Shack LCD readout temperature sensor (Archer catalog number 277-0123). Temperature readings with both probes were in good agreement.

Results and Discussion

The titration approach was applied to an aquifer material sample (sample tube number 13, Sample K-61, collected 4-6-90, depth 11 feet 5 inches to 11 feet 10 inches below the surface) taken from the Columbus Air Force Base site. The sample had been stored in the dry state, with no attempt to exclude oxygen. Thus the sample was well-oxidized. The sample was sieved dry through standard sieves to separate it into well-defined size fractions consisting of particle sizes > 850 μm, 425 - 850 μm, 250 - 425 μm, 106 - 250 μm, 75 - 106 μm, and < 75 μm. The fraction in the size range < 75 μm diameter was selected for titration to evaluate the spectroelectrochemical coulometric titration protocol for this aquifer material. This size fraction constituted 14.3 % by weight of the total sample weight, as determined by sieving. This percentage was nearly double the weight percent determined by sieving at the time of collection (8.63 %), although the percentages of other size fractions were in accordance with the as-sampled values. This behavior suggests that the particles aggregate to a significant extent, and that the percent of fine particles measured is significantly dependent on the degree of disturbance of the particles during sieving.

The pH of a suspension of < 75 μm diameter aquifer material in 5 mL of distilled water without added buffer was in the range of 5.1, depending on solids loading, stirring, and other factors. However, because the optical absorption properties and solubility of resorufin were not favorable at or below pH 6, samples were prepared for titration in a pH 7 phosphate buffer, with 0.1 ionic strength. The pH of a 1.2 % by weight suspension of aquifer material in pH 7.0 phosphate buffer was 7.03, indicating that the buffer capacity of the buffer was sufficient to control the pH of the suspension.

Spectroelectrochemical coulometric titrations were carried out in the controlled potential mode, at an applied potential of -0.65 V vs. Ag/AgCl/1 M KCl reference electrode. This potential was sufficiently negative that methyl viologen (MV^{2+}), the component with the most negative reduction potential, was reduced to the radical cation ($MV^{+\cdot}$), while any components

with more positive reduction potentials which could react directly with the electrode also were reduced. Methyl viologen could also react homogeneously with titratable components which do not react readily directly with the electrode surface. The reaction is thus catalytic, in the sense that reaction of $MV^{+\cdot}$ with species of more positive reduction potentials accelerates their reduction and regenerates MV^{2+} for further reaction. Upon addition of the desired quantity of charge, the applied potential was disconnected, and the potentiostat was placed in the potentiometric mode at zero current. While any oxidized species with reduction potentials more positive than that of methyl viologen remained in the system, any initial excess of $MV^{+\cdot}$ was consumed, and the system was allowed to come to equilibrium. Excess $MV^{+\cdot}$ remained in solution after equilibrium was reached, only after all species with more positive reduction potentials had been reduced. The appearance of excess $MV^{+\cdot}$ thus indicated the end of the titration.

Experiments were first carried out on a solution containing all of the reagents (10.1 micromolar resorufin, 0.408 millimolar methyl viologen) and the pH 7.0, ionic strength 0.1 phosphate buffer, but not the aquifer material. The resulting plot of absorbances at the wavelengths characteristic of resorufin (572 nm) and of methyl viologen radical cation (396 nm) is shown in Figure 2A. In all cases, absorbances are recorded in dual-wavelength difference mode with respect to the absorbance at 800 nm. Difference measurements are extremely valuable in compensating for the effects of scattered light, settling of suspension over time in the cell, and other nonidealities, since none of the species under study absorb appreciably at 800 nm, and the apparent absorbance at this wavelength is still affected by light scattering and other nonidealities, in a manner analogous to that at the analytically useful wavelengths of 572 and 396 nm. A plot of the potentiometric electrode potential vs. charge is shown in Figure 2B. The initial lag before resorufin is titrated is due to residual oxygen (ca. 3.5 μM, ca. 1 % of the ambient concentration prior to degassing and analysis) not completely removed during the degassing process. The quantity of residual oxygen varied, but the quantity of resorufin was consistent from run to run. It is clear in Figure 2A that there is essentially no break between completion of titration of resorufin and initiation of titration of methyl viologen. This behavior is to be expected for the system in absence of aquifer material, since the reduction potentials of resorufin and methyl viologen are in the order observed. The potentiometric potential seen in

Figure 2B also follows the trend expected, initially being governed by the redox equilibrium between oxidized and reduced components of resorufin, and then shifting to a value governed by the equilibrium between methyl viologen dication and methyl viologen monocation.

The weight percent of aquifer material in suspension during titrations was selected empirically based on the maximum quantity of suspended solids which afforded an acceptable level of light scattering. For the experiments reported here, the solids loading was 0.0426 % by weight. This loading afforded a slightly turbid solution with light scattering levels that were still acceptable. (Absorbance was elevated ca. 0.2 absorbance units at 396 nm relative to the same solution composition in absence of aquifer material.) A slightly higher loading level (perhaps threefold higher) would have been feasible if the spectrophotometer had had better stray light characteristics. The results of a spectroelectrochemical titration of an 0.0426 % by weight suspension of aquifer material under the same solution conditions as Figure 2A are shown in Figure 3A. The only difference evident between the response for the aquifer suspension and the blank control is a slightly lower residual oxygen content (ca. 0.7 % of the initial ambient concentration prior to degassing). In addition, the vertical shift of the absorbance of both curves in Figure 3A at ca. 3 mcoul charge reflects reoxidation of reduced resorufin during a waiting period of more than two hours before the next increment of charge was added, to test the susceptibility of the measurements to oxygen leakage over long periods. While some further improvements in preventing oxygen leaks would be beneficial, the observed leakage rate corresponds to the relatively low quantity of ca. 0.65 nmol O_2 per hour into the cell. After correction for the need to rereduce the resorufin that was reoxidized during this period, the charge consumed during titration of resorufin is in close agreement with the charge required for the blank, and the onset of excess $MV^{+\cdot}$ generation coincides closely with the completion of titration of resorufin. The plot of potentiometric potential vs. charge in the presence of sediment, seen in Fig. 3B, also corresponds closely to that for the blank in absence of sediment, except that the initial potential is more negative as a result of more effective degassing and oxygen removal.

The data support the conclusions reached previously that spectroelectrochemical titrations can be successfully applied to the investigation of redox capacity of soils. However, the aquifer sample represents a lower limit of the applicability of the technique with the solids loading used

here. The oxidative redox capacity of the aquifer material is so low that it cannot be resolved with respect to the relative uncertainty of the charge measurements. It can be estimated, however, based on the uncertainty of charge measurements, which is certainly less than 0.25 mcoul, that the oxidative redox capacity of this system is less than 3 microequivalents per gram of aquifer material. This is in the lower range reported by Heron et al. (2), but considerably lower than the values reported by Barcelona and Holm (1). Thus an upper limit can be established for the oxidative redox capacity of this aquifer material sample. This is considerably smaller than the results obtained from a very iron rich and organic carbon rich pond sediment investigated previously (3,4), which had an oxidative capacity of ca. 700 μequiv/g sediment for a particle size range smaller than 2 μm average diameter. The use of significantly larger particles in this sample is probably a factor, since there is evidence to suggest that the titratable oxidant in this aquifer material may be available iron (III) species, which are presumably distributed over the surface of sediment particles. Since surface area grows inversely in proportion to particle diameter, with a 1/r dependence if the particles can be treated as hard spheres, or a $1/r^{0.6}$ dependence if the particles are fractal (8), it is likely that these larger particles will inherently have a smaller redox capacity in mequiv/gram of sediment than the smaller particles used previously, but it is also clear that the oxidant loading per unit area of particle in the Columbus aquifer material is inherently lower than in the Beaver Dam sediment previously studied (3.4). Preliminary evidence from other workers at Tyndall Air Force Base suggests that the iron content of the Columbus aquifer material is also significantly lower than that of the Beaver Dam sediment. Clearly the relation between iron and redox capacity will need to be explored in greater depth.

Experiments to assess the temperature dependence of pressure in a closed vessel were carried out between the temperatures of 13 °C and 36 °C. The change dV in the volume of a closed vessel can be expressed as a function of changes in the pressure dp and temperature dT of the system, as given by the expression:

$$dV = \partial V/\partial p)_{T,c}\, dp + \partial V/\partial T)_{p,c}\, dT = (V/K_c)\, dp + \alpha_c\, V\, dT, \qquad (1)$$

where V is the initial volume at specified initial temperature and pressure, K_c is the bulk elastic modulus of the container material, and α_c is the volumetric coefficient of thermal expansion of the container material. The corresponding expression for the liquid sample in the container is:

$$dV = - \partial V/\partial p)_{T,l}\, dp + \partial V/\partial T)_{p,l}\, dT = - (V/K_l)\, dp + \alpha_l\, V\, dT, \qquad (2)$$

where K_l is the bulk elastic modulus of the liquid, and α_l is the volumetric coefficient of thermal expansion of the liquid. The pressure coefficient terms have opposite signs in equations (1) and (2), because an increase in internal pressure inside the container tends to increase the internal volume of the container, but tends to decrease the volume of the liquid contained therein. Equating the volume changes for container and liquid, equations (1) and (2) can be combined to yield the following expression for pressure change as a function of temperature:

$$dp = \frac{\alpha_l - \alpha_c}{\frac{1}{K_c} + \frac{1}{K_l}}\, dT \qquad (3)$$

The values of the parameters used were obtained from Perry and Chilton's *Chemical Engineering Handbook* (9): $\alpha_c = 4.80 \times 10^{-5}$ (°C)$^{-1}$ for stainless steel; $K_c = 2.8 \times 10^7$ pounds per square inch (psi) for stainless steel, and $K_l = 2.989 \times 10^5$ psi for water. The thermal expansion coefficient of the liquid was given by the expression

$$\alpha_l = a_1 + 2\, a_2\, T + 3\, a_3\, T^2, \qquad (4)$$

where $a_1 = -5.96 \times 10^{-5}$ (°C)$^{-1}$, $a_2 = 7.91 \times 10^{-6}$ (°C)$^{-2}$, and $a_3 = -4.09 \times 10^{-8}$ (°C)$^{-3}$, which were obtained from regression analysis of the temperature dependence of the thermal expansion coefficient of water over the range from 0 - 35 °C (9).

The predicted pressure change relative to an initial temperature of 25 °C was calculated by substituting equation (4) for the temperature dependence of α_l directly in equation (3) and by integrating equation (3) with respect to temperature from 25 °C to the temperature of measurement. Figure 4 illustrates the remarkable pressure change of 930 psi over the ca. 22 °C temperature range between 13.8 and 35.4 °C. Such a large pressure change implies that use of a closed cell in a thermally unregulated spectrophotometer will inevitably lead to leakage (or even destruction of the cell) unless a solution expansion volume is provided. Also shown in Figure 4 is a plot predicting the pressure change based on the known thermal expansion coefficients of water. The shape of the experimental plot of pressure vs. temperature is in good qualitative agreement with the shape predicted based on the thermal expansion coefficient of

water. The predicted pressure range is slightly greater than the observed change, but the predicted curve merges completely with the experimental curve if the predicted pressure range is normalized to the observed pressure range.

Conclusions

It was established that the Columbus aquifer material had a very low oxidation capacity, with an estimated upper limit of ca. 3 μequiv/g of sediment. This result is on the order of the lower redox capacity samples investigated by Heron (2), and considerably lower than the levels reported by Barcelona and Holm for similar aquifer materials (1), or reported by us for pond sediments (3,4). These results give support to the contention by Heron et al. that the results of Barcelona and Holm may be too high. We were able to establish that the use of absorbance measurements for indirect quantitation by monitoring of an optical reporter molecule is insufficiently sensitive to provide reliable quantitation at the redox capacity levels characteristic of Columbus aquifer material. The problem of insufficient resolution of the redox capacity of Columbus aquifer material must be resolved for further progress to be made. The most promising approach is to switch from absorbance as the optical probe to fluorescence. The detection limit of the method described here is limited by the quantity of sediment loading which can be tolerated while still obtaining acceptable absorbance signals. Fluorescence measurements are considerably more immune to light scatter, enabling considerably higher solids loading. We propose for future work to utilize fluorescence detection to improve the attainable resolution and thereby resolve the redox capacity of Columbus aquifer material.

It was also established that astonishingly high pressures can be generated in closed vessels completely filled with liquid, if temperature is not carefully regulated. These results make it clear that vessels used in experiments on liquids must have sufficient compressible volume, whether as a gas phase or a compressible insert (e. g. rubber or other elastic material), to allow liquid expansion without generation of ruinous internal pressures. Such volumes may be very modest, on the order of less than 10 μL, to eliminate this potential problem.

Acknowledgements

We wish to thank the Air Force Office of Scientific Research Summer Faculty Program

for financial support and the staff of the Environics Division, Armstrong Laboratory, Tyndall Air Force Base, for their hospitality and support of our research project. Particular thanks are extended to David Burris, Eila Burr, Tim Campbell, Chris Antworth, and William MacIntyre for their help and encouragement.

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Figure 1. Electrochemical Titration Cell Diagram

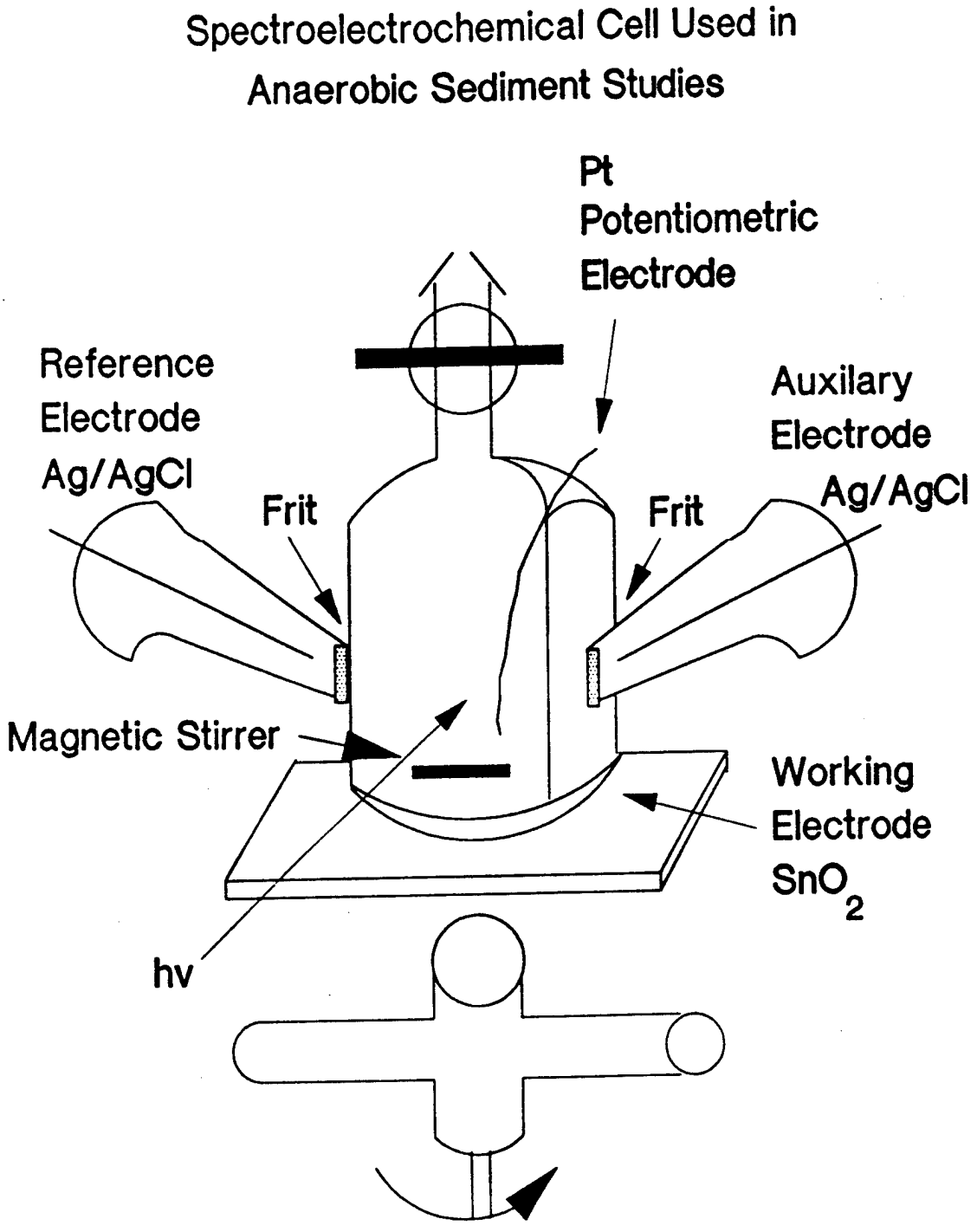
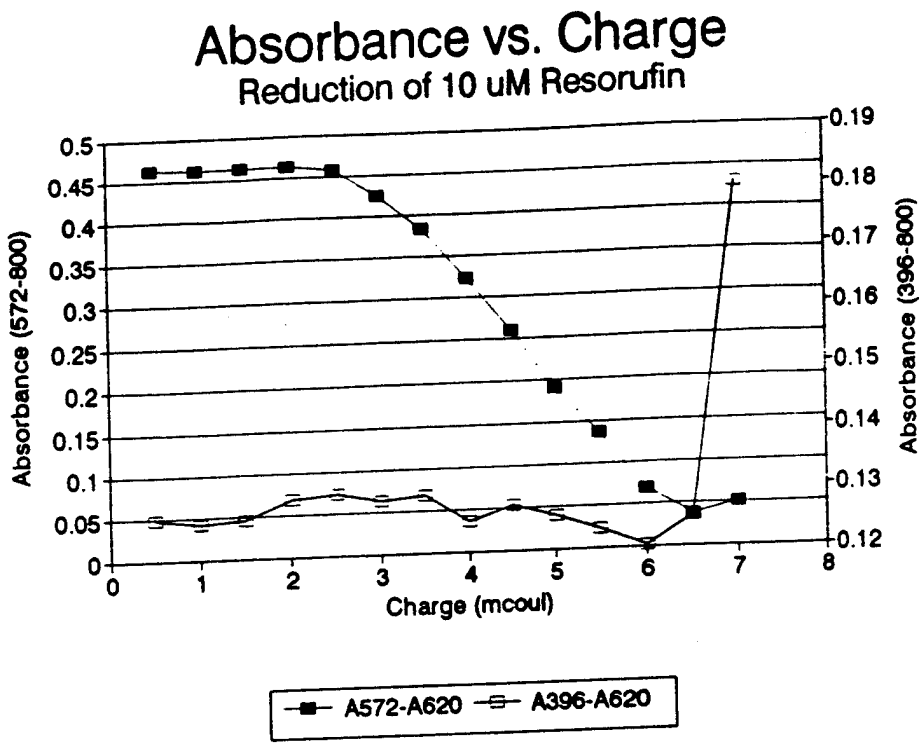


Figure 2. Spectroelectrochemical Titration Plots - Blank Run

A. Absorbance vs. Charge

B. Potentiometric Potential vs. Charge



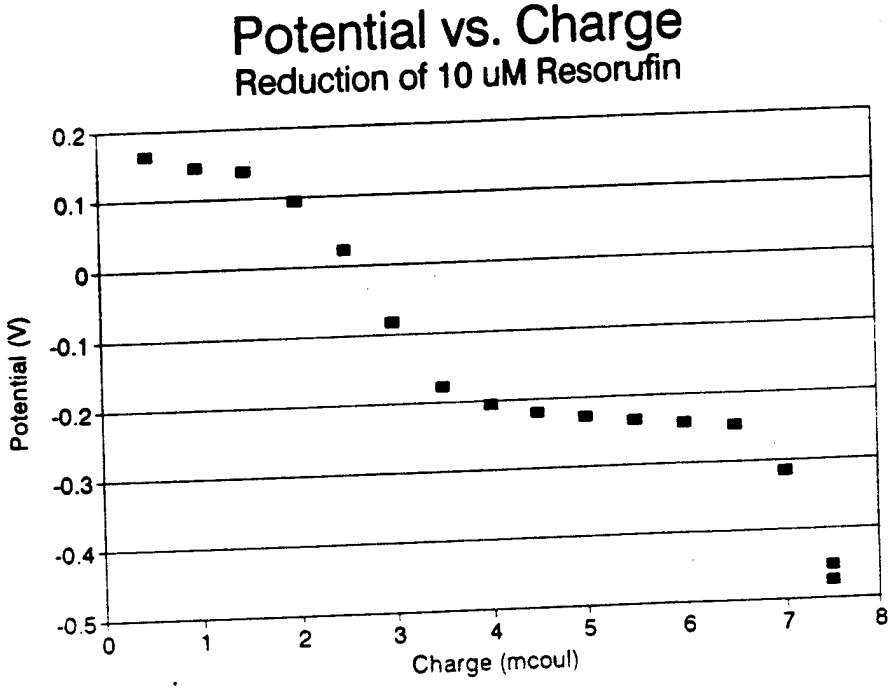
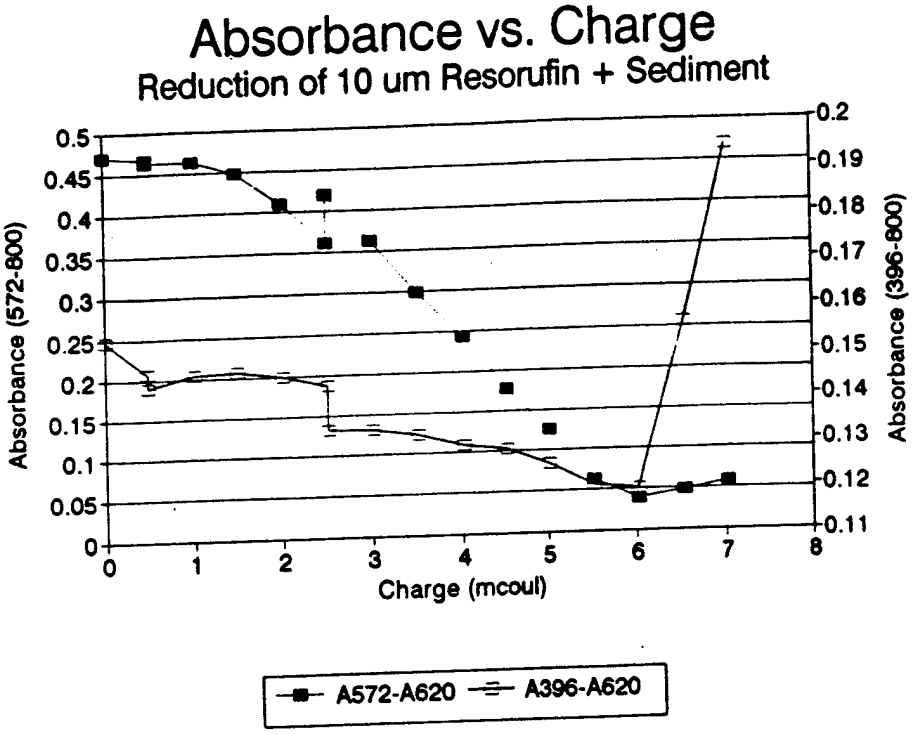


Figure 3. Spectroelectrochemical Titration Plots - Columbus Sediment Run

A. Absorbance vs. Charge

B. Potentiometric Potential vs. Charge



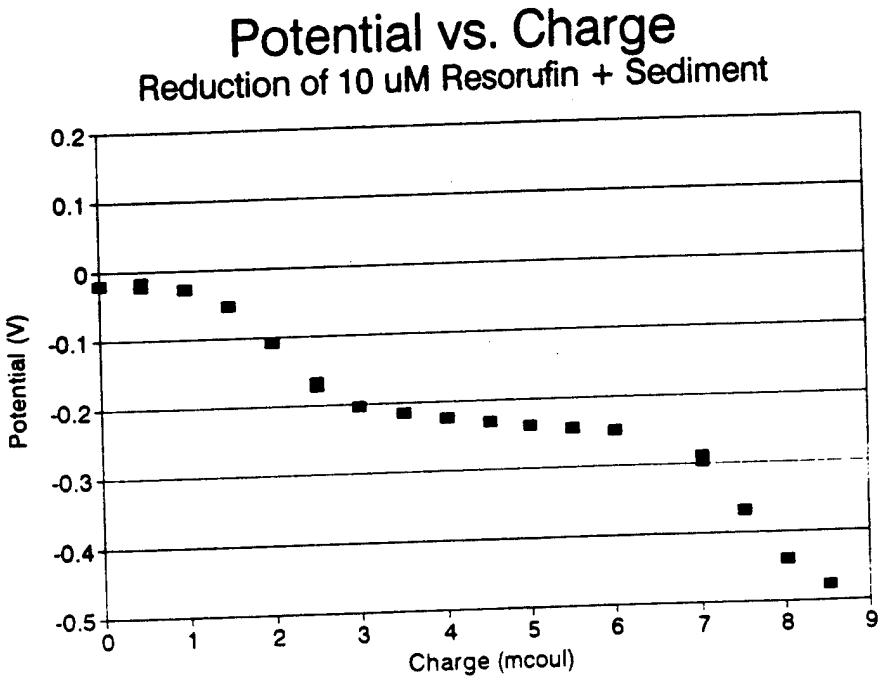


Figure 4. Temperature Dependence of Pressure in a Closed Vessel of Water