

This publication has been superseded by ODP Technical Note 15:
http://www-odp.tamu.edu/publications/tnotes/tn15/f_chem1.htm

WATER CHEMISTRY PROCEDURES ABOARD JOIDES RESOLUTION - SOME COMMENTS

Joris Gieskes
Scripps Institution of Oceanography
La Jolla, California 92093

Gail Peretsman
Ocean Drilling Program
Texas A&M University
College Station, Texas 77843-3469

OCEAN DRILLING PROGRAM
TEXAS A&M UNIVERSITY

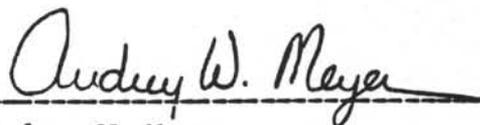
TECHNICAL NOTE
NUMBER 5
MAY 1986



Philip D. Rabinowitz
Director



Louis E. Garrison
Deputy Director



Audrey W. Meyer
Manager of Science Operations

Material in this publication may be copied without restraint for library, abstract service, educational or personal research purposes; however, republication of any portion requires the written consent of the Director, Ocean Drilling Program, Texas A&M University, College Station, Texas 77843-3469, as well as appropriate acknowledgement of this source.

Technical Note No. 5
First Printing 1986

Distribution

Copies of this publication may be obtained from the Director, Ocean Drilling Program, Texas A&M University, College Station, Texas 77843-3469. In some case, orders for copies may require payment for postage and handling.

DISCLAIMER

This publication was prepared by the Ocean Drilling Program, Texas A&M University, as an account of work performed under the international Ocean Drilling Program which is managed by Joint Oceanographic Institutions, Inc., under contract with the National Science Foundation. Funding for the program is provided by the following agencies:

Department of Energy, Mines and Resources (Canada)
Deutsche Forschungsgemeinschaft (Federal Republic of Germany)
Institut Francais de Recherche por l'Exploitation de la Mer (France)
Ocean Research Institute of the University of Tokyo (Japan)
National Science Foundation (United States)
Natural Environment Research Council (United Kingdom)
European Science Foundation Consortium for the Ocean Drilling Program
(Belgium, Denmark, Finland, Iceland, Italy, Greece, the Netherlands,
Norway, Spain, Sweden, Switzerland and Turkey)

Any opinions, findings and conclusions or recommendations expressed in this publication are those of the author(s) and do not necessarily reflect the views of the National Science Foundation, the participating agencies, Joint Oceanographic Institutions, Inc., or Texas A&M University Research Foundation.

PREFACE

"This will revolutionize geochemistry at sea," was the reaction of Dennis Graham, a chemistry technician with a long history in DSDP chemistry programs, after working—on the shakedown cruise, Leg 100 of the Ocean Drilling Program—in the Chemistry Laboratory of JOIDES Resolution. One of the main prerequisites for scientific advancement has always been the access to modern instrumentation, and the geochemical veteran cited above acknowledged the effort of ODP to provide a state-of-the-art laboratory for chemical work at the locus of interest: **the drill site**. Surpassing the main concern of shipboard organic geochemistry in previous phases of scientific ocean drilling, i.e. safety monitoring for hydrocarbons, geochemists onboard JOIDES Resolution are now able to analyze almost every property of sediments and rocks, ephemeral and resident, according to the modern analytical and data handling standards.

The following Technical Note is one of a series of three on geochemistry onboard JOIDES Resolution +). The demand for a concise description of tasks and supporting infrastructure for geochemical work onboard ship was the immediate reason for writing this series. Equally important was the desire to standardize methodology and to document geochemical work performed in the previous phases of scientific ocean drilling. They are intended to provide a guideline for shipboard geochemists, in order to facilitate their various duties.

The chemistry laboratory owes its tremendous potential to the advice and help of numerous individuals, who provided invaluable assistance in design and set-up. ODP acknowledges, in particular, the efforts of Drs. J.H. Brooks and M.C. Kennicutt II (Oceanography Department, Texas A&M University) in the planning stage; of Bradley Julson and Dennis Graham (ODP) for their activities toward setting up the laboratory in its present great shape; of Drs. Keith Kvenvolden (U.S.G.S., Menlo Park), Joris Gieskes (Scripps Institution of Oceanography), Kay Emeis (ODP), Mr. Thomas McDonald (Oceanography Dept., TAMU), and Ms. Gail Peretsman (ODP), who were responsible for setting up the methods and procedures for the chemistry laboratories and writing these reports; and of Ms. Katie Sigler, Ms. Gail Peretsman, Ms. Tamara Frank, Mr. Matt Mefferd, Mr. Larry Bernstein, and Mr. Bradley Julson, for their roles in the maintenance and operation of the chemistry equipment at sea. Without the efforts of all of the above persons, the chemistry at sea program would not have reached its present highly successful state.

- +) Gieskes, J.M., and Peretsman, G., 1986. Water Chemistry Procedures aboard JOIDES Resolution. ODP Technical Note #5.
Kvenvolden, K.A., and McDonald, T.J., 1986. Organic Geochemistry on the JOIDES Resolution — An Assay. ODP Technical Note #6.
Emeis, K.-C., and Kvenvolden, K.A., 1986. Shipboard Organic Geochemistry on JOIDES Resolution. ODP Technical Note #7.



Philip D. Rabinowitz, Director
May 1986

WATER CHEMISTRY PROCEDURES ABOARD JOIDES RESOLUTION—SOME COMMENTS

TABLE OF CONTENTS

	Page
I. Introduction	1
II. Standards	1
III. Analytical Methods	1
A. Wet-Chemical Methods	1
1. Chloride	1
a. Reagents	4
b. Procedure	4
c. Units	4
2. Calcium	4
a. Introduction	4
b. Reagents	4
c. Procedure	5
3. Magnesium	5
a. Introduction	5
b. Reagents	6
c. Procedure	6
d. Calculations	6
B. Instrumental Methods	8
1. Introduction	8
2. Metrohm Autotitrator	8
a. Alkalinity Analysis	8
(1) Introduction	8
(2) Methodology	10
(3) Data Evaluation	10
(4) Standardization	10
(5) General Remarks	15
b. Chlorinity Analysis	15
3. Dionex Ion Chromatography	15
a. Introduction	15
b. Sample Preparation	20
c. Analytical Results	20
(1) Calcium and Magnesium	20
(2) Sulfate	20
(3) Potassium	20
4. Spectrophotometric Methods	30
a. Introduction	30
b. Analytical Procedures and Results	30
(1) Ammonia	30
(a) Introduction	30
(b) Reagents	30

TABLE OF CONTENTS—Continued

	Page
(c) Procedure	30
(2) Nitrite	35
(a) Introduction	35
(b) Reagents	35
(c) Procedure	35
(d) Standards	35
(3) Nitrate	36
(a) Introduction	36
(b) Reagents	37
(c) Procedure	37
(d) Standards	37
(4) Silica	37
(a) Introduction	37
(b) Reagents	37
(c) Standards	38
(d) Method	39
(5) Phosphate	40
(a) Introduction	40
(b) Reagents	40
(c) Procedure	40
(6) Bromide	41
(a) Introduction	41
(b) Stock solutions	41
(c) Freshly made solutions	41
(d) Standard solutions	41
(e) Procedure	42
(7) An Important Note of Caution	42
IV. Sampling Strategies	42
V. Acknowledgments	43
VI. References	45

LIST OF FIGURES

Figure	Page
1. Alkalinity determination, based on Gran function plotted vs. volume HCl. Sample is IAPSO standard seawater, measured on Metrohm autotitrator.	11
2. Alkalinity determination, based on Gran function plotted vs. volume HCl. Sample is surface seawater, measured on Metrohm autotitrator.	13
3. Chlorinity determination, based on plot of EMF (millivolts) vs. volume of AgNO ₃ . Sample is IAPSO standard seawater, measured on Metrohm autotitrator.	17
4. Chlorinity determination, based on plot of EMF (millivolts) vs. volume of AgNO ₃ . Sample is surface seawater, measured on Metrohm autotitrator.	19
5. Calcium standard curve, from Dionex Ion Chromatograph analysis of Joris standards and IAPSO standard seawater.	23
6. Magnesium standard curve, from Dionex Ion Chromatograph analysis of Joris standards and IAPSO standard seawater.	25
7. Sulfate standard curve, from Dionex Ion Chromatograph analysis of Joris standards and IAPSO standard seawater.	29
8. Potassium standard curve, from Dionex Ion Chromatograph analysis of Joris standards and IAPSO standard seawater.	33

LIST OF TABLES

Table		Page
1.	Recipe for artificial JOIDES standards.	2
2.	Composition of standards (mM).	3
3.	Comparison between Ca^{2+} and Mg^{2+} obtained by "direct" procedures and the "super" Ca-method (see text).	7
4.	Proposed buffer standards.	9
5.	Dionex analysis for Ca^{2+} and Mg^{2+} using standard solutions.	21
6.	Dionex analysis for SO_4^{2-} using standard solutions.	27
7.	Dionex standardization for K^+ using standard solutions.	31
8.	Sample distribution of interstitial waters.	44

I. INTRODUCTION

During Leg 102 of the Ocean Drilling Program, a unique opportunity arose to study the various chemical procedures available on the SEDCO/BP-471 (JOIDES Resolution). In the following we describe the various procedures used during ODP Leg 102, together with an evaluation of their accuracy and usefulness in the shipboard chemistry lab. We try to distinguish between wet chemical titration methods and instrumental methods (Dionex Ion Chromatograph, Brinkmann Autotitrator Spectrophotometer). Although, no doubt, new methods will become available in the future, we hope that the present report will serve as a base from which shipboard geochemistry on interstitial waters may develop.

II. STANDARDS

The primary standard for water analysis on the ship remains IAPSO standard seawater. However, for the purpose of expanding standards we prepared in La Jolla a set of six standards (Joris 1-6) with varying composition of the major constituents Ca^{2+} , Mg^{2+} , K^+ , SO_4^{2-} , and Cl^- . The method of preparation is presented in Table 1, and if necessary, can be used to expand the present standards to cover any concentration range. The standards were analyzed by wet chemical methods and atomic absorption spectrophotometry at Scripps by Abe Espiritu and onboard the JOIDES Resolution by Gieskes. The average compositions obtained by these analysts are presented in Table 2, including estimated errors. These standards were used throughout this investigation for reference.

III. ANALYTICAL METHODS

For the analysis of Ca^{2+} , Mg^{2+} , and Cl^- (Gieskes and Lawrence, 1976) these methods were also used routinely on the Glomar Challenger during a large portion of the Deep Sea Drilling Project (DSDP), since Leg 35. On the JOIDES Resolution wet-chemical titrations will still have to be used routinely, because there is often a lack of time, or a failure of laboratory instruments. Thus it is important to ensure the availability of titration equipment and chemicals, and the proper training of the chemistry technicians. The use of these methods was important on Leg 101, for example, when over 100 samples were analyzed using wet chemical methods.

The wet chemical titrations recommended for shipboard analyses, including improvements to earlier methodology, are detailed below.

A. WET-CHEMICAL METHODS

1. Chloride

The determination of chloride is of primary importance in interstitial water work, especially for the following reasons: (a) Small but important increases in chloride have been observed with depth in the sediments (upper 100

Table 1. Recipe for artificial JOIDES standards

Standard	A	B	C	D
Joris 1	230	2.5	15	2.5
Joris 2	233	5.0	10	2.0
Joris 3	236	7.5	5	1.5
Joris 4	236.5	10.0	2.5	1.0
Joris 5	235.8	12.5	1.2	0.5
Joris 6	235	15.0	0	0

Standards with higher calcium concentrations can be made with appropriate amounts of A and B. Standardization of such new standards can be achieved with the "super" calcium titration (see text).

- A. 2 L of about 0.5 M NaCl (about 29 g NaCl/L)
- B. About 1 M CaCl₂ (about 11 g CaCl₂/100 cm³)
- C. About 1 M MgSO₄ (about 25 g MgSO₄·7H₂O/100 cm³)
- D. About 1 M KCl (about 7.5 g KCl/100 cm³).

Table 2. Composition of Standards (mM).

	Ca ²⁺	Mg ²⁺	SO ₄ ²⁻	K ⁺	Cl ⁻
IAPSO	10.55	54.0	28.9	10.44	559
Joris 1	7.24	61.4	61.4	10.2	492
Joris 2	14.66	40.9	40.9	8.1	508
Joris 3	22.2	19.4	19.4	6.3	524
Joris 4	29.2	10.0	10.0	4.1	544
Joris 5	36.4	4.5	4.5	2.0	550
Joris 6	43.7	0.0	0.0	0.0	561
Accuracy	<u>+0.5%</u>	<u>+1-2%</u>	<u>+1%</u>	<u>+2%</u>	<u>+0.4%</u>

Analysts: Joris Gieskes and Abe Espiritu, Scripps Institution of Oceanography, La Jolla, CA 92093

m or so) in open ocean sites. These changes can be related to glacial caused salinity changes (McDuff, 1985). The changes amount only to about 2‰ and therefore an accuracy of at least 0.4‰, and preferably better, is imperative.

(b) Best estimates of Na^+ concentrations rely on charge balance considerations, and, therefore, the accuracy of the Cl^- determination is of great importance.

a. Reagents

Silver Nitrate: Make an 0.1 M AgNO_3 (16.8 g-dm^{-3}), solution in distilled water.

Indicator: Dissolve 4.2 g A.R. potassium chromate and 0.7 g A.R. potassium di-chromate in 100 cm^3 distilled water.

b. Procedure

Pipette 0.1 cm^3 of sample into a 15 cm glass beaker and add about 5 cm^3 of distilled water. Add 0.1 cm^3 of indicator solution. Under vigorous stirring (magnetic stirrer) and with the burette tip immersed (Gilmont burette) titrate until a faintly reddish-brown color is observed (silver chromate) and stays permanent. Standardize with IAPSO standard seawater ($\text{Cl} = 19.376 \text{ g-kg}^{-1}$; 559 mM). The color change is somewhat subjective, but the same operator can achieve great accuracies, i.e., better than 0.4‰.

c. Units

There is a tendency to express chloride concentration as chlorinity, i.e., grams of chloride per kilogram of water. We advocate abandoning this habit, primarily because most other concentrations are expressed in molar units. Secondly, we measure everything volumetrically and densities of pore waters are not precisely known. We therefore suggest using moles per volume, or millimoles per dm^3 , henceforth called mM. Any worries about other halogens being included are not important, as these halogens constitute less than 0.1% of the total halide concentration.

2. Calcium

a. Introduction

Calcium was determined using the mini-version of the method of Tsunogai, Nishimura and Nakaya (1968). In this method, ethylene-bis-(oxyethylene-nitrilo)-tetra-acetic acid (EGTA) is used as a titrant, and 2,2'-ethane-diylidene-dinitrilo-diphenol (GHA) is used as an indicator. The calcium-GHA complex is extracted quantitatively into a layer of n-butanol.

b. Reagents

A stock solution of 0.1M EGTA is prepared by dissolving 3.8 g EGTA in 30 cm^3 of 1M NaOH and diluting to 100 cm^3 . From this, a 10 millimolar (mM) solution of EGTA is prepared by appropriate dilution. Standardization is achieved by means of Wormley IAPSO seawater.

Borate Buffer: 5 g borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) and 15 g sodium hydroxide are dissolved in 250 cm^3 distilled water.

GHA: 40 mg GHA are dissolved in 100 cm^3 of ethanol. Prepare a fresh batch before each site.

c. Procedure

Transfer, preferably using an Eppendorf pipette, 0.5 cm^3 of sample into a 15 cm^3 titration vessel and add about 2-3 cm^3 of distilled water. While stirring the solution (magnetic stirrer), add 0.5 cm^3 of 0.04% GHA and 0.5 cm^3 of buffer solution. Stir for about 3 minutes. In the case of high calcium concentration, start titrating right away so that color will not fade before the end of the titration. Titrate with a 10-mM EGTA solution, using a micro-burette with immersed tip while stirring vigorously. When the reddish color starts to disappear, add 2 cm^3 of butanol. Near the endpoint, stirring should be stopped frequently, in order to observe the color of the butanol layer. The endpoint is characterized by a change from red to colorless or to a yellowish color similar to the lower solution.

Tsunogai et al. (1968) report that in seawater serious interference can occur as a result of co-precipitation of Ca^{2+} in the $\text{Mg}(\text{OH})_2$ precipitate. This problem can be averted if, prior to the addition of the borax buffer, about 95% or more of the necessary EGTA is added. Values measured using this 95% "super" method to analyze standard seawater ($\text{Mg}/\text{Ca} = 5.5$) differ from the "direct" method by about 6%. The difference between experimental values rapidly diminishes with decreased Mg/Ca , as is commonly observed in interstitial waters (Gieskes, 1983). For these reasons the direct-titration method is preferred over the 95% method, particularly because sufficient interstitial water is commonly not available. A correction can be carried out for the direct-titration calcium determination, usually in conjunction with the EDTA titration for total alkaline earths and the subsequent derivation of the Mg concentration.

If standardization occurs with IAPSO standard seawater ($\text{Ca}/\text{Cl} = 0.0213$ $\text{g}\cdot\text{kg}^{-1}$ chlorinity) then it should be remembered that the concentration of Ca^{2+} in standard seawater is 10.55 mM. Any interference by Sr^{2+} is largely taken care of by the inclusion of seawater strontium in the titer. Analysis of the standard seawater should employ the same titration method as that used for the samples.

3. Magnesium

a. Introduction

In order to obtain the value of dissolved Mg^{2+} a titration is carried out for total alkaline earths, i.e., Ca^{2+} , Mg^{2+} and Sr^{2+} (other contributors being trivial). Then the value for $\text{Ca}^{2+} + \text{Sr}^{2+}$ is subtracted or rather, if the "direct" Ca^{2+} titration is used, the formulae given below are used. If the 95% plus "super" method is used for Ca^{2+} , subtraction of Ca^{2+} from the total alkaline earths will suffice.

b. Reagents

EDTA: Dissolve ca. 15 g of EDTA (sodium salt) in 1 dm³ of distilled water to yield an approximately 0.03 M solution. Add 1 cm³ of a 50 mM MgCl₂ solution to the EDTA.

Buffer: 67.5 g of NH₄Cl and 570 cm³ NH₄OH are dissolved in water and the final volume is made up to 1 dm³.

Indicator: 0.05 g of Eriochrome Black-T is dissolved in 50 cm³ of 80% ethanol solution. Before each site, a fresh batch of 50 cm³ should be prepared.

c. Procedure

To a 0.5 cm³ sample, add 5 cm³ of distilled water. Add 1 cm³ ammonia buffer and 0.1 cm³ indicator solution. Start stirring (magnetic stirrer). Color change is red to blue. If no Mg²⁺ is present in the solution the Mg²⁺ in the EDTA (not part of the titration) guarantees the color change. Reproducibility is about 0.5%, accuracy about 1%.

Standardization is carried out with IAPSO seawater, using Ca/Cl and Sr/Cl ratios of Culkin (1965) and Mg/Cl of Carpenter and Manella (1973). For standard seawater with a chlorinity of 19.375 g/kg, this yields 64.54 mM.

d. Calculations

Gieskes and Lawrence (1976) suggested two simple formulas for the calculation of Ca²⁺ and Mg²⁺ for the "direct" Ca²⁺ and alkaline earth determinations. On the basis of new titrations carried out aboard the JOIDES Resolution (Table 3) we have developed two more precise formulas for this purpose. Denoting total alkaline earths by D_t, and the "direct" Ca²⁺ titration value by Ca_t, we obtain the corrected Mg and Ca values as follows:

$$\text{Mg}_{\text{corr}} = (D_t - 0.94\text{Ca}_t)/1.01;$$

$$\text{Ca}_{\text{corr}} = 0.94\text{Ca}_t + 0.01 \text{Mg}_{\text{corr}}.$$

As can be seen from Table 3, these formulas yield good agreement with the data obtained by the more perfect Ca-"super" method.

Eventually, when data on dissolved Sr²⁺ are available minor corrections can be made for this component according to the formulas

$$\text{Ca}^{2+}_{\text{final}} = \text{Ca}_{\text{corr}} - 0.8 \text{Sr}^{2+} + 0.08;$$

$$\text{Mg}^{2+}_{\text{final}} = \text{Mg}_{\text{corr}} + 0.2 \text{Sr}^{2+}.$$

However, Sr²⁺ hardly ever exceeds concentrations of 1 mM, so that corrections are usually trivial and well within the accuracy of the determinations. In addition, Sr²⁺ at seawater concentrations (0.09 mM) is included in the titer.

Table 3. Comparison between Ca²⁺ and Mg²⁺ obtained by "direct" procedures and the "Super" Ca-method (see text)

Sample	Ca _t ¹⁾ mM	Ca _{corr} ²⁾ mM	Ca _{super} ³⁾ mM	Ca+Mg mM	Mg _t ¹⁾ mM	Mg _{corr} ²⁾ mM	Mg _{super} ³⁾ mM
Joris 1	7.24	7.24	7.29	68.87	61.63	61.45	61.58
Joris 2	14.96	14.47	14.65	55.38	40.42	40.91	40.75
Joris 3	23.02	21.84	21.99	41.68	18.66	19.84	19.69
Joris 4	30.85	29.10	29.11	39.17	8.32	10.07	10.07
Joris 5	38.45	36.19	36.23	40.85	2.4	4.66	4.62
Joris 6	46.39	43.61	43.55	43.89	-3.6	-0.12	-0.78

1) No correction, standardization with IAPSO.

2) Corrected with the formulas

$$Mg_{corr} = (D_t - 0.94 Ca_t) / 1.01$$

$$Ca_{corr} = 0.94 Ca_t + 0.01 Mg_{corr}$$

$$\text{where } D_t = Ca_{2+} + Mg^{2+}$$

3) Ca_{super} obtained from method that uses >95% EGTA added prior to buffer addition (see text), called "super" method

$$Mg_{super} = D_t - Ca_{super}$$

B. INSTRUMENTAL METHODS

1. Introduction

In this section, we will discuss both the alkalinity method, employing the Metrohm autotitrator, as well as the methods for Ca^{2+} , Mg^{2+} , SO_4^{2-} and K^+ analyses which use the Dionex Ion Chromatograph. We attempted Ca/Mg titrations with the Metrohm, but they were time-consuming and electrode behavior was erratic (a Corning glass reference electrode and a Brinkmann ion specific electrode were used). We do not think this is a fast and reliable method and it should not be used in favor of simple colorimetric titrations or the Dionex method. This section also includes a discussion of spectrophotometric methods used for determination of nitrate, ammonia, silica and dissolved iron.

2. Metrohm Autotitrator

a. **Alkalinity Analysis**

(1) Introduction

The use of the Metrohm titrator for alkalinity is indeed an improvement over the procedures used previously. Of course, the best feature of the system is the Brinkmann combination pH electrode, which proved to be very reliable and steady. A small problem, however, is that a significant amount of KCl leaks into the solution, thus rendering the sample dubious for potassium determination.

During Leg 102 we found that the computer-generated alkalinity curve produced for each analysis produced little useful information. During Leg 110 the program was changed to plot Gran function vs. amount of acid added. The modified program now yields not only the Gran factor for each analysis, but provides information on the reliability of the linear least squaring carried out by the computer.

Standardization of the electrodes should not be carried out too often. The electrodes do not react well to the large changes in ionic strength that they encounter each time they are immersed in the various buffer solutions. It is preferable to leave the electrodes well conditioned in slightly acidified seawater prior to their use in the titrations.

Standardization of the electrodes and the evaluation of the pH of the sample are determined using NBS (National Bureau of Standards) pH buffers, which, of course, are based on the NBS pH scale. However, because the standards are made in dilute solutions, subsequent introduction of the electrodes into saline solutions often leads drift over long time intervals. A recent subpanel meeting of the Joint Panel on Oceanographic Tables and Standards has advocated the adoption of a new pH scale, utilizing buffers designed specifically for use in media with ionic strengths similar to those of seawater. Two of these pH standards are described in Table 4. These standards can then be used not only for the determination of the pH, but also for the evaluation of the electrode slope.

Table 4. Proposed buffer standards.¹

$p_{m_H}(S)$ values for Standard A (Tris buffer)								
Salinity	5°C	10°C	15°C	20°C	25°C	30°C	35°C	40°C
30	8.798	8.635	8.479	8.330	8.187	8.050	7.917	7.789
35	8.812	8.649	8.493	8.343	8.200	8.062	7.929	7.801
40	8.826	8.663	8.507	8.357	8.214	8.076	7.943	7.815

$p_{m_H}(S)$ values for Standard B (Bis buffer)								
Salinity	5°C	10°C	15°C	20°C	25°C	30°C	35°C	40°C
20	9.509	9.341	9.178	9.022	8.873	8.729	8.588	8.453
35	9.574	9.404	9.241	9.084	8.934	8.788	8.647	8.512
45	9.599	9.430	9.267	9.110	8.960	8.814	8.673	8.538

¹As interstitial waters usually show large changes in composition, we will rely on the "free" hydrogen ion concentration scale (Bates and Culberson, 1977), where m_H is the concentration of free hydrogen ions in mol/Kg-H₂O and where we denote $-\log m_H$ with the symbol p_{m_H} .

In 1000 g of synthetic seawater dissolve:

A: 0.02 moles (2.423 g) "Tris" B: 0.02 moles (2.103 g) "Bis"
 0.02 moles (3.152 g) Tris.HCl 0.02 moles (2.832 g) Bis.HCl

NOTE: Tris = Tris(hydroxymethyl)aminomethane (2-amino-2-[hydroxymethyl]-2,3-propanediol); Bis = Bis(hydroxymethyl)methylaminomethane (2-amino-2-methyl-1,3-propanediol).

Tris, Tris.HCl, and Bis are obtainable commercially (for example, from Sigma Chemical Co., St. Louis, MO 63178). Bis.HCl can be crystallized from a concentrated solution of Bis that has been neutralized with purified hydrochloric acid.

The synthetic seawater can be prepared from NaCl, KCl, CaCl₂, MgCl₂, and Na₂SO₄ according to formulas given elsewhere (for example, Khoo et al., 1977; Bates and Calais, 1981). Recrystallization of the NaCl used in preparing the synthetic seawaters is advisable, in order to eliminate traces of acidic and basic contaminants that might alter the standard values of p_{m_H} .

A final note of caution needs to be issued with respect to the reported pH. During sample retrieval on board ship, often substantial gas losses can occur, which would severely affect the pH, but not the alkalinity. At very low CO₂ contents on the other hand, CO₂ uptake into the sample may occur, and this, again, will affect the pH and not the alkalinity. For these reasons the use of pH for equilibrium calculations is limited.

(2) Methodology

When enough interstitial water is available, use 10 cm³ for the titration; when less is available, use 5 cm³ or even as little as 3 cm³. When very little is available, skip the titration altogether. In that case, determination of other constituents is more important.

(3) Data Evaluation

The computer uses the Gran function to evaluate the alkalinity as follows:

$$F = (V + V_0) 10^{E/a}$$

where V₀ = original volume of sample; V = volume of acid added; E = electromotive force (millivolts); a = slope of electrodes - experimental.

Subsequently, F can be plotted vs. volume of acid added, or the computer can evaluate the regression function and extrapolate to F = 0. At F = 0, the volume of acid added is representative of the alkalinity.

A few typical Gran plots are presented in Figures 1 and 2. Please note the occasional "flyer" in the Gran function (must be instrumental). However, this demonstrates that a computer plot of the Gran function is necessary—the computer can choose its own x-axis for proper scaling.

The data suggest that one can get accuracies to about +3%, which is quite adequate for this type of titration. The difference in slope in Figure 1 was probably due to the recurrent use of NBS buffers. The final results, however, were within 2.1%. It does suggest that leaving the electrodes in a constant medium is advisable. The use of the newly proposed buffers will alleviate this situation.

(4) Standardization

At the beginning of a cruise, it is a good idea to make a few NaHCO₃ standard solutions, ranging in alkalinity from 2.5 mM to 25 mM. These standards should be prepared in about 0.7 M KCl in order to imitate the ionic strength of seawater. These standards will give you the actual normality of the acid. Subsequently, you can take a clean surface seawater sample in a clean Nalgene flask, 1 to 2 dm³ in volume, which can then serve as a reference standard for the cruise.

When we ran standards of about 2.5 mM, we found a reproducibility of 2% in the standard. Regular checks with the reference seawater standard will be an important check on the accuracy of the analysis.

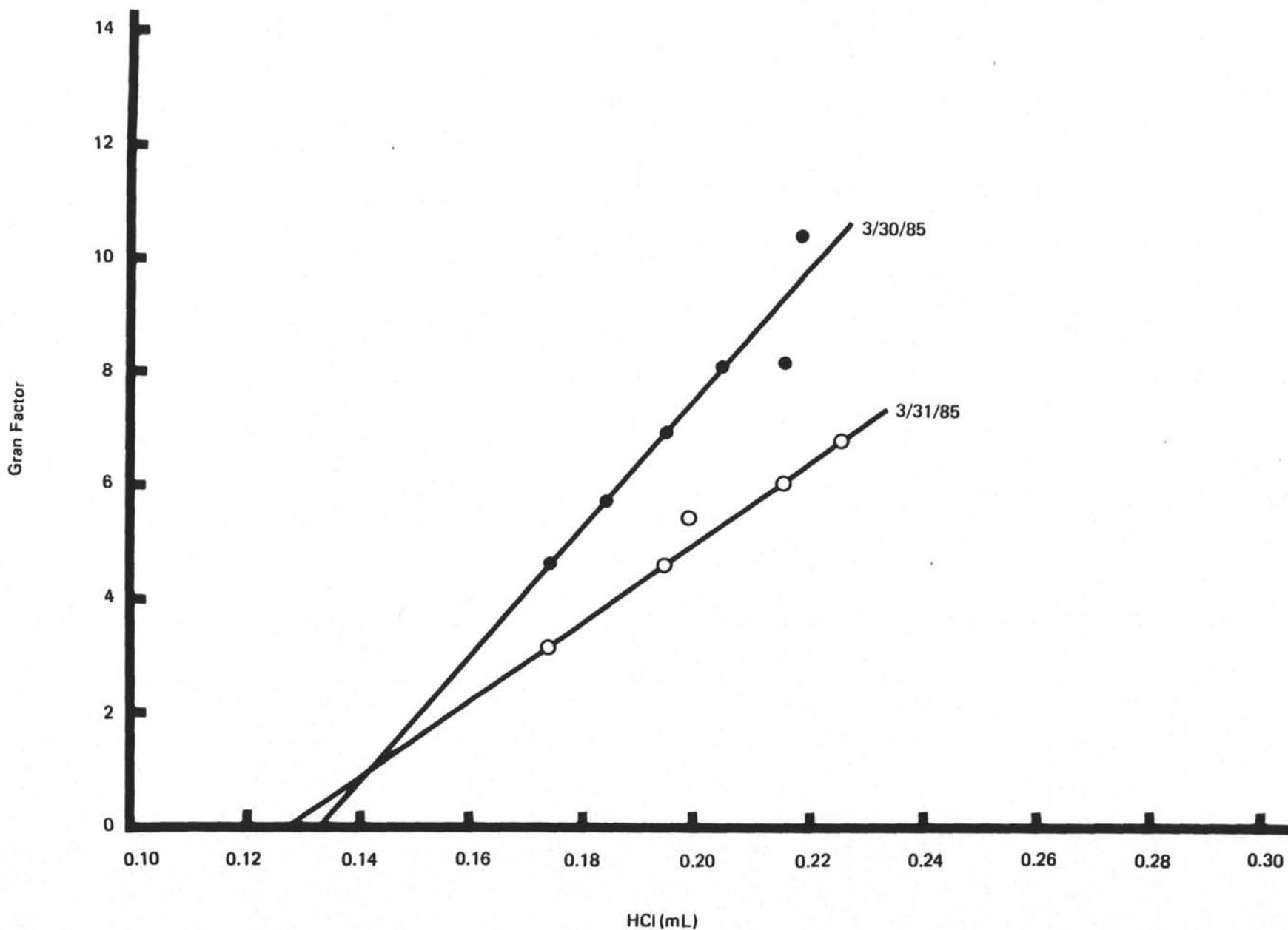


Figure 1. Alkalinity determination, based on Gran function plotted vs. volume HCl. Sample is IAPSO standard seawater, measured on Metrohm autotitrator.

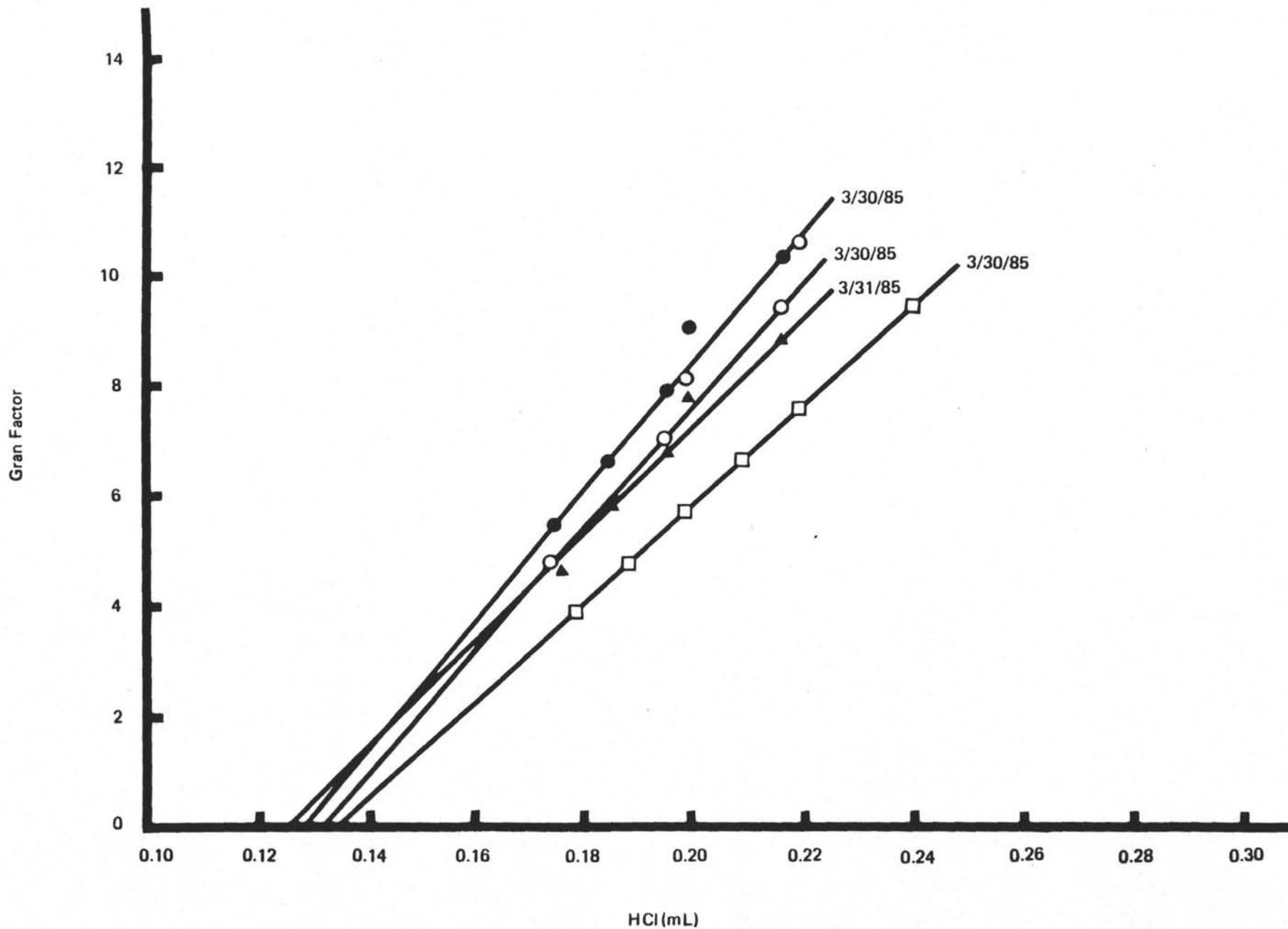


Figure 2. Alkalinity determination, based on Gran function plotted vs. volume HCl. Sample is surface seawater, measured on Metrohm autotitrator.

Normally, titrations are carried out with a 0.1-M HCl solution.

(5) General Remarks

Alkalinity used to be expressed in terms of milli-equivalents per unit volume ($\text{meq}\cdot\text{dm}^{-3}$). This use has been abandoned under the newly adopted SI system, and alkalinity is henceforth expressed in millimoles (of acid equivalent), i.e., mM. Note that the old $\text{meq}\cdot\text{dm}^{-3}$ is equivalent to the unit mM.

In open-ocean settings sample quantities of 5 or 10 cm^3 will require the use of a reasonable amount of acid, perhaps at most 1 or 2 cm^3 , whereas in near shore settings alkalinities may rise to extremely high values, up to 125 mM. In the case of the latter, the volume of acid may approach the volume of the sample, resulting in large dilution factors. Nonetheless, one can do a good titration and the sample retains its usefulness for further analysis. Of course, a stronger HCl solution (e.g., 0.5 M HCl) will be advantageous for these high alkalinity solutions.

Always record on the stored alkalinity sample the quantity titrated as well as the total amount of acid used in the titration, as this provides the dilution factor for future work on the sample.

b. Chlorinity Analysis

We explored the applicability of the electrometric titration method for chloride. In this method we used 0.1 cm^3 of sample, with 5 cm^3 of low-conductivity water and 0.1 cm^3 of chromate/dichromate indicator.

The results of IAPSO analyses are presented in Figures 3 and 4. The two endpoints agree well with each other, yielding essentially identical results. Based on these two titrations, agreement for standard seawater is very satisfactory, i.e., about $\pm 0.5\%$.

Any automation of the method should rely on the initial change in electromotive force (emf) which starts to change about 0.05 cm^3 before the equivalent point.

3. Dionex Ion Chromatography

a. Introduction

Initial analysis attempts on the Dionex Ion Chromatograph were based on Wescan experience on DSDP Leg 92 (Gieskes). On that cruise, we were forced to produce actual peaks on graph paper; reasonably successful quantification was obtained by plotting peak height vs. concentration (c.f. Wescan Report, Leg 92).

During ODP Leg 102 a similar plot was attempted from the results of the Dionex, with unsatisfactory results. Areas were too small to be reliable and peak height was only marginally useful. By further experimentation, it became clear that the best plan was to actually create peaks that ran off the integrator paper, but gave large areas from the integrator run report. The

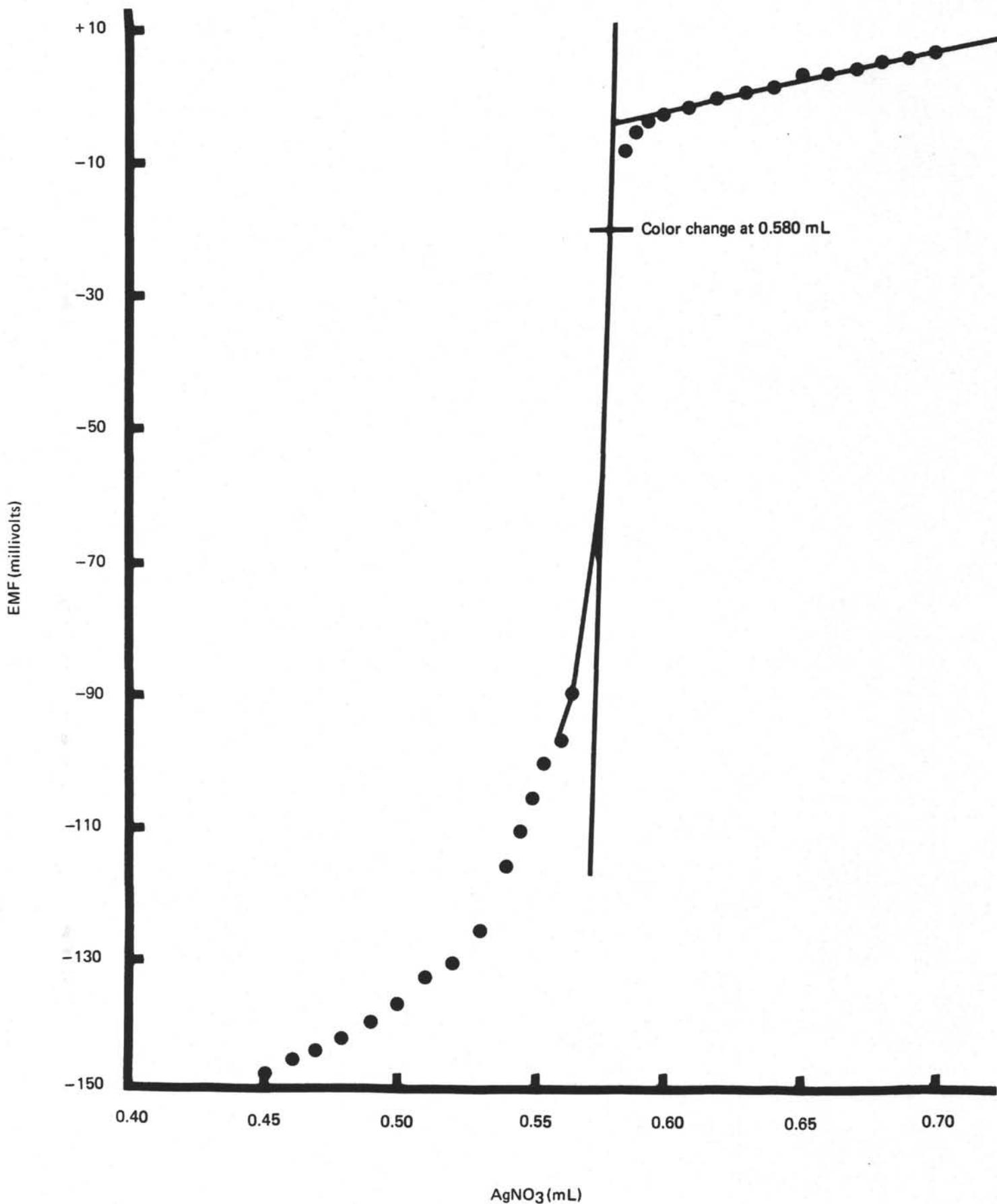


Figure 3. Chlorinity determination, based on plot of EMF (millivolts) vs. volume of AgNO_3 . Sample is IAPSO standard seawater, measured on Metrohm autotitrator.

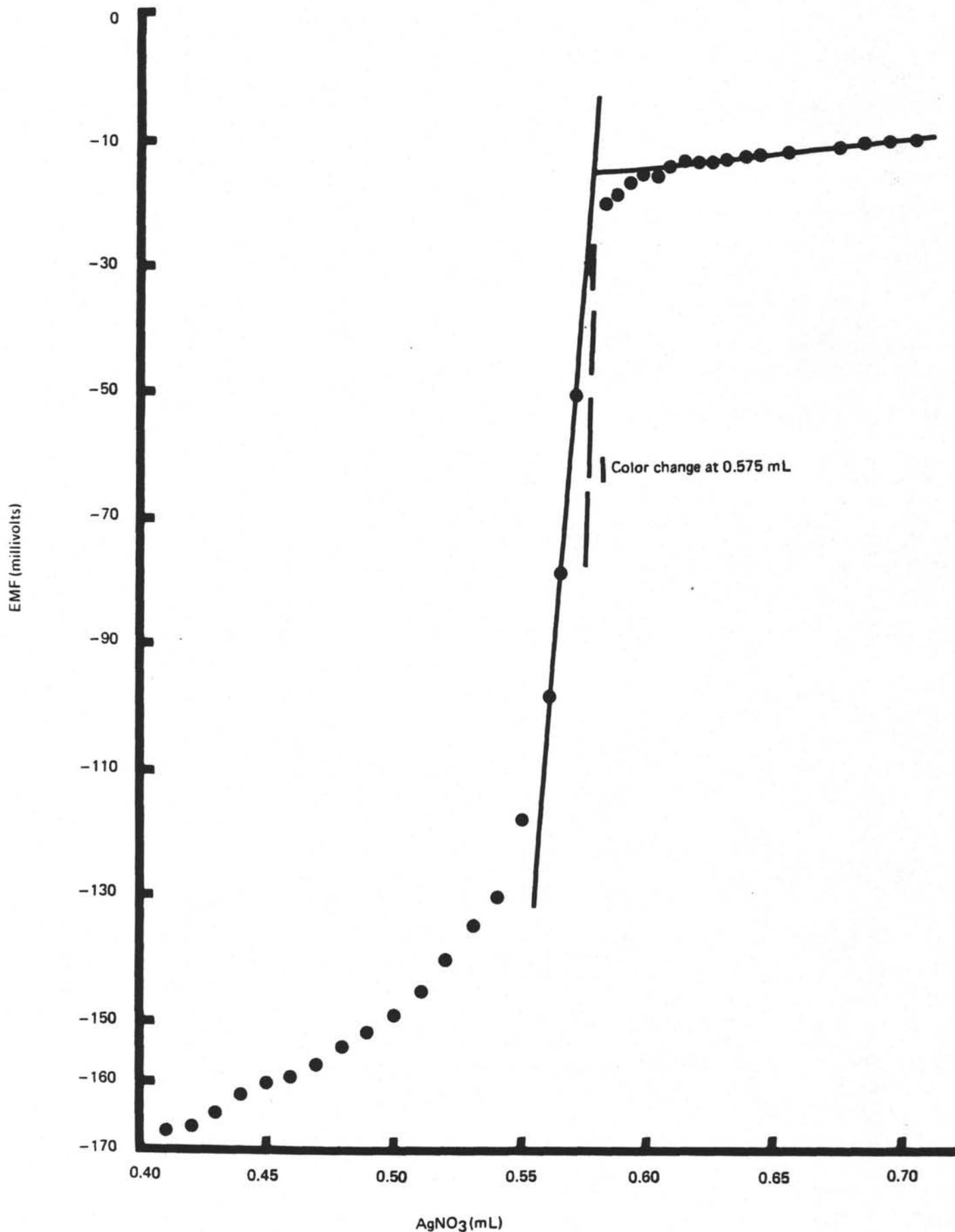


Figure 4. Chlorinity determination, based on plot of EMF (millivolts) vs. volume of AgNO_3 . Sample is surface seawater, measured on Metrohm autotitrator.

methods developed below, with the exception of that for K^+ , used the large peak area concept with very satisfactory results. For K^+ equal success may be in reach, but limited time precluded further experimentation with the monovalent system.

Below, each of the methods used is described including an estimate of accuracy based principally of the standards prepared from both IAPSO, and from the six Joris standards.

b. Sample Preparation

All analyses were carried out on a 0.2 cm^3 sample diluted to 100 cm^3 with low conductivity water. Storage in clean plastic containers is recommended. The small sample size is one of the chief advantages of the Dionex method.

c. Analytical Results

(1) Calcium and Magnesium

Calcium and magnesium data and instrumental conditions are presented in Table 5. For standardization, use was made of IAPSO at various dilutions (normalized to 0.2 cm^3 per 100 cm^3), of the six Joris standards, and of the downhole samples BAW-1, BAW-2A, and BAW-2B, recovered during Leg 102 (see Salisbury, Scott, Auroux, et al., in press for more information on downhole samples).

The results from the I.C. analyses are summarized in Table 5 and in Figures 5 and 6.

In both cases, good standard curves are obtained, with non-linear behavior limited to the lower concentration ranges, i.e., in the range where areas become very small. This problem may be alleviated by choosing either a smaller attenuation or a lower range setting. However, with proper calibration, reasonably accurate measurements of both Ca^{2+} and Mg^{2+} are possible, to within about 2% error for Mg^{2+} , and to a slightly smaller margin of error for Ca^{2+} .

For practical purposes, we recommend interspersing of standards that approximate the range of the samples being analyzed. Keep in mind that concentration depth trends are reasonably predictable in most cases.

(2) Sulfate

Sulfate data and instrumental conditions are presented in Table 6. Standardization was based on analyses of IAPSO and Joris standards. During sulfate analysis an unidentified peak eluted at 4.6 minutes; it only occurred in the IAPSO analysis. This is presumably a bicarbonate (alkalinity) peak.

The sulfate standard curve is presented in Figure 7. It shows very good linearity. There is therefore no doubt that the Dionex provides a very accurate measure of SO_4^{2-} .

(3) Potassium

As mentioned before, optimal conditions for the determination of K^+ were not obtained. We do recommend that the method be explored further. A good

Table 5. Dionex analysis for Ca²⁺ and Mg²⁺ using standard solutions.

Sample	Ca ²⁺		Mg ²⁺	
	mM	Area counts* (x 10 ⁶)	mM	Area counts* (x 10 ⁶)
Joris 1	7.24	1.72 ± 0.07	61.4	21.70 ± 0.15
Joris 2	14.66	3.95 ± 0.10	40.9	14.44 ± 0.08
Joris 3	22.17	6.63 ± 0.19	19.4	6.20 ± 0.07
Joris 4	29.24	9.18 ± 0.09	10.0	2.90 ± 0.06
Joris 5	36.40	11.72 ± 0.08	4.5	1.20 ± 0.04
Joris 6	43.68	14.85 ± 0.15	0	—
IAPSO 0.2	10.55	2.60 ± 0.08	54.0	18.7 ± 0.10
IAPSO 0.16	8.44	1.90 ± 0.10	43.2	14.56 ± 0.02
IAPSO 0.1	5.28	1.32	27.0	9.07
BAW-1	12.17	3.08	55.4	18.64
BAW-2A	47.0	15.08	39.1	13.2
BAW-2B	48.7	16.00	37.6	12.8

Operating Parameters

Instrumental

Pressure = 450 psi
 Flow rate = 2.2 cm³/s
 Range = 30 uS
 Retention times:
 2.59 min = Mg²⁺
 4.60 min = Ca²⁺

Integrator

Zero = 0, 154.85
 Att = 2
 Cht sp = 1.0
 Pk wd = 0.50
 Thrsh = 0
 Ar rej = 5000

* Note: Area counts represent the average of three runs per standard, with the operating parameters given above. Values of area counts vary considerably over time, even with identical operating parameters, owing to changes in instrumental conditions (e.g., column age). For this reason, analysts should not try to duplicate the area-count values listed here. Rather, they should define, for each standard, current values that are reproducible and that yield linear graphs when plotted against concentration.

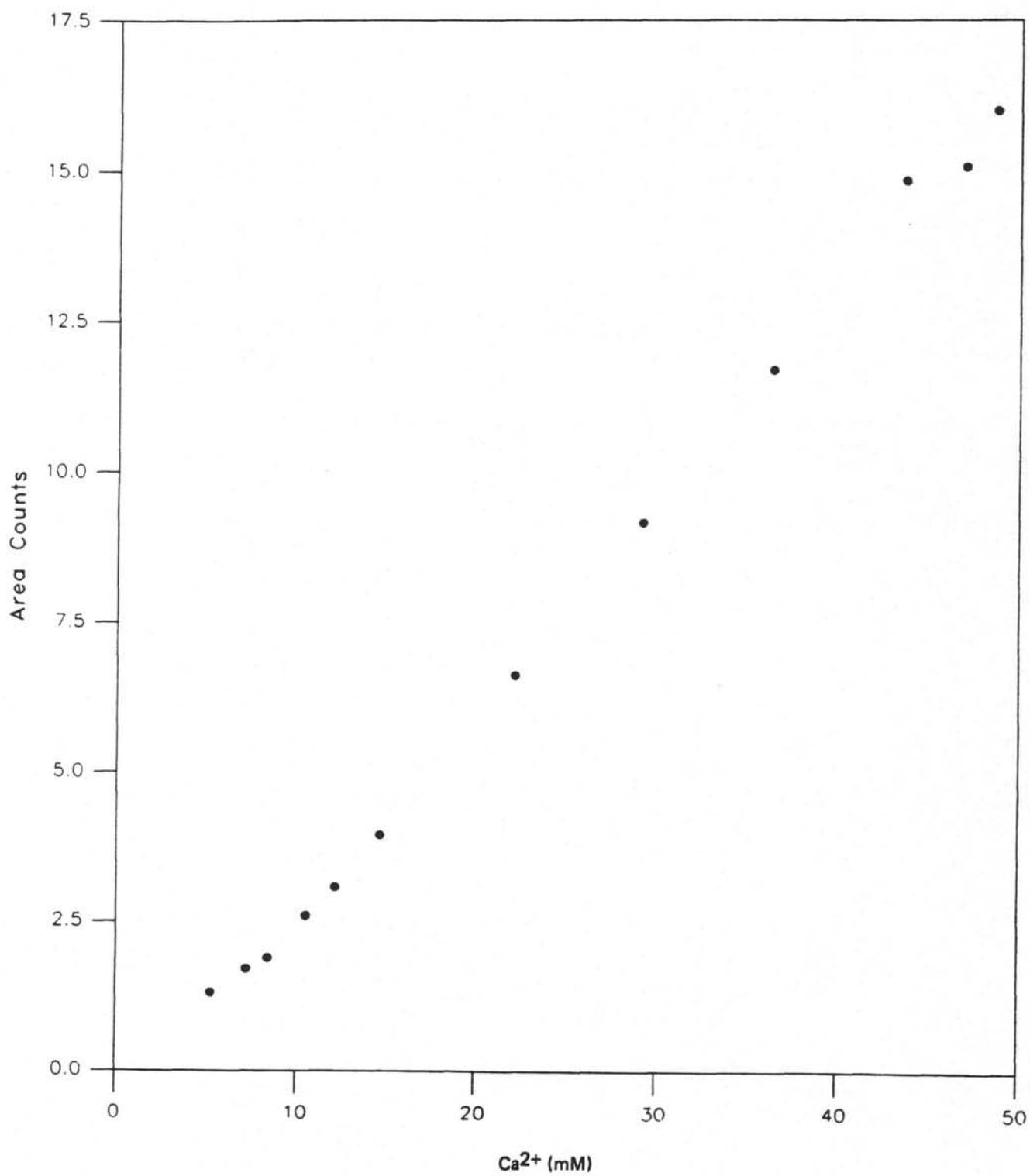


Figure 5. Calcium standard curve, from Dionex Ion Chromatograph analysis of Joris standards and IAPSO standard seawater.

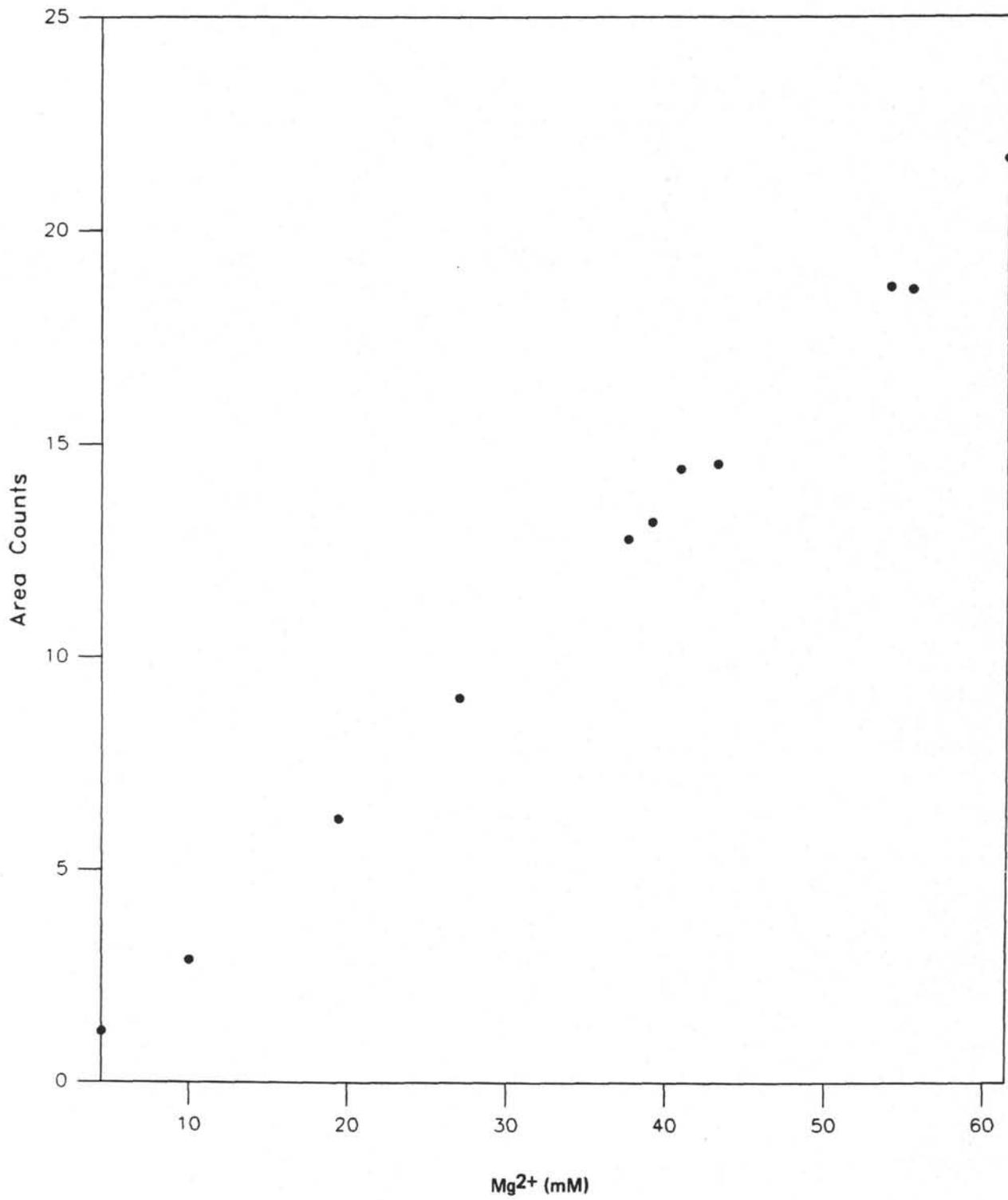


Figure 6. Magnesium standard curve, from Dionex Ion Chromatograph analysis of Joris standards and IAPSO standard seawater.

Table 6. Dionex analysis for SO_4^{2-} using standard solutions.

Sample	mM	Area counts* ($\times 10^6$)
Joris 1	61.4	23.74 \pm 0.20
Joris 2	40.9	16.04 \pm 0.02
Joris 3	19.4	7.50 \pm 0.24
Joris 4	10.0	4.15 \pm 0.35
Joris 5	4.5	1.90 \pm 0.05
Joris 6	0.0	0.0
IAPSO 0.2	28.9	11.35 \pm 0.20
IAPSO 0.16	23.12	8.90 \pm 0.30
IAPSO 0.1	14.45	5.69

Operating Parameters

Instrumental

Pressure = 110 psi
 Flow rate = 2.3 cm^3/s
 Range = 30 μS
 Retention times:
 4.60 min = ?
 7.70 min = SO_4^-

Integrator

Zero = 0, -2.54
 Att = 3
 Cht sp = 1.0
 Pk wd = 0.50
 Thrsh = 0
 Ar rej = 5000

* Note: Area counts represent the average of three runs per standard, with the operating parameters given above. Values of area counts vary considerably over time, even with identical operating parameters, owing to changes in instrumental conditions (e.g., column age). For this reason, analysts should not try to duplicate the area-count values listed here. Rather, they should define, for each standard, current values that are reproducible and that yield linear graphs when plotted against concentration.

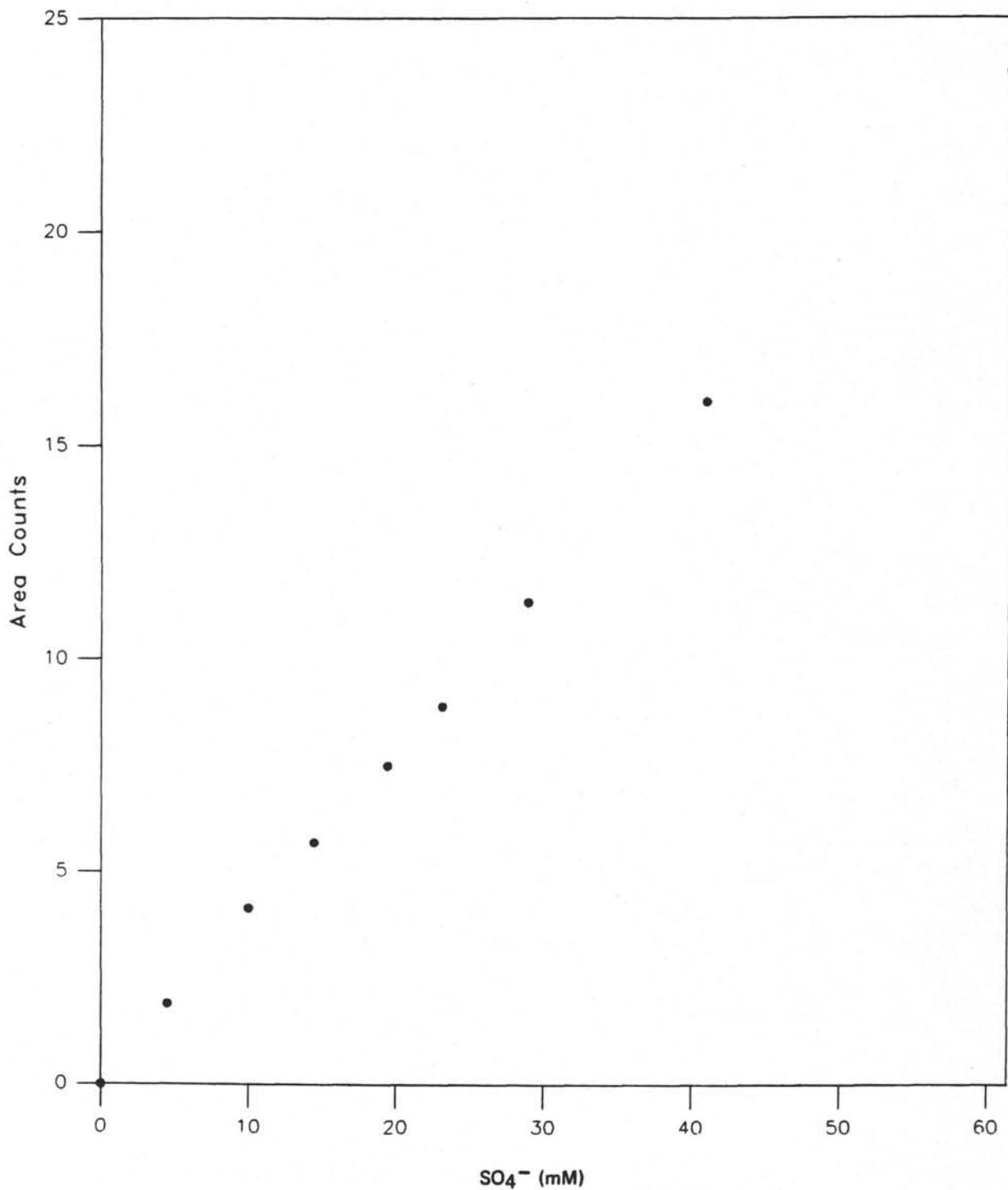


Figure 7. Sulfate standard curve, from Dionex Ion Chromatograph analysis of Joris standards and IAPSO standard seawater.

idea may be to work with higher concentrations (e.g., 0.5 cm³ sample diluted to 100 cm³ with pure low conductivity water) and/or lower attenuations and output range.

The data are summarized in Table 7, and the standard curve is presented in Figure 8. As a first approximation, the accuracy is tolerable, but it took an enormous amount of effort to get the method this far.

4. Spectrophotometric Methods

a. Introduction

One of us (Gieskes) brought along a Gilford 300-N microsample spectrophotometer to be used on ship for the determination of nitrate, ammonia, silica, and dissolved iron in the waters recovered during Leg 102. More recently a Bausch and Lomb Spectrophotometer was added to the shipboard chemistry lab and was tested during Leg 110. The methodologies summarized below are suitable for either instrument.

b. Analytical Procedures and Results

(1) Ammonia

(a) Introduction

Ammonia concentrations can vary over a wide range in deep drill holes. Whereas in the open ocean sites concentration ranges are from 0 to 1000 micromolar, organic carbon-rich, rapidly accumulating sediments can show concentrations up to 30 mM (Gieskes, 1983). Thus standards and aliquots for the determination of ammonia must be adopted to the situation at hand. As the method described below is very fast, necessary adjustments of methodologies can be accomplished rapidly. The method is basically that described by Solorzano (1969).

(b) Reagents

Phenol-alcohol solution: dissolve 0.8 g reagent-grade phenol in 100 cm³ 95% ethyl alcohol (make fresh each day).

Sodium nitroprusside solution: dissolve 0.15 g sodium nitroprusside (sodium nitroferricyanide) in 200 cm³ deionized water (make fresh each day).

Alkaline solution: dissolve 7.5 g trisodium citrate and 0.4 g NaOH in 500 cm³ deionized water. This is a fairly stable solution.

Oxidizing solution: add 1 cm³ fresh sodium hypochlorite (4% available chlorine) to 50 cm³ alkaline solution and use the same day. However, chlorox will do the same job.

Ammonia standard: dissolve 5.345 g A.R. ammonium chloride, dried overnight at 100°C, in 1 dm³ deionized water. This is a 0.1 molar NH₃ stock solution and is diluted with deionized water for use.

(c) Procedure

Use a 100 lambda Eppendorf pipette to transfer 0.1 cm³ of each sample to a

Table 7. Dionex standardization for K^+ using standard solutions.

Sample	mM	Area counts* (x 10 ⁵)
IAPSO 0.2	10.44	16.4; 17.3
Joris 2	8.1	12.1; 13.6
Joris 3	6.3	9.4

Operating Parameters

Instrumental

Pressure = 450 psi
 Flow rate = 2.0 cm³/s
 Range = 30 uS
 Retention times:
 7.60 min = K^+

Integrator

Zero = 0, 0.27
 Att = 3
 Cht sp = 1.0
 Pk wd = 0.50
 Thrsh = 0
 Ar rej = 5000

* Note: Area counts represent the average of three runs per standard, with the operating parameters given above. Values of area counts vary considerably over time, even with identical operating parameters, owing to changes in instrumental conditions (e.g., column age). For this reason, analysts should not try to duplicate the area-count values listed here. Rather, they should define, for each standard, current values that are reproducible and that yield linear graphs when plotted against concentration.

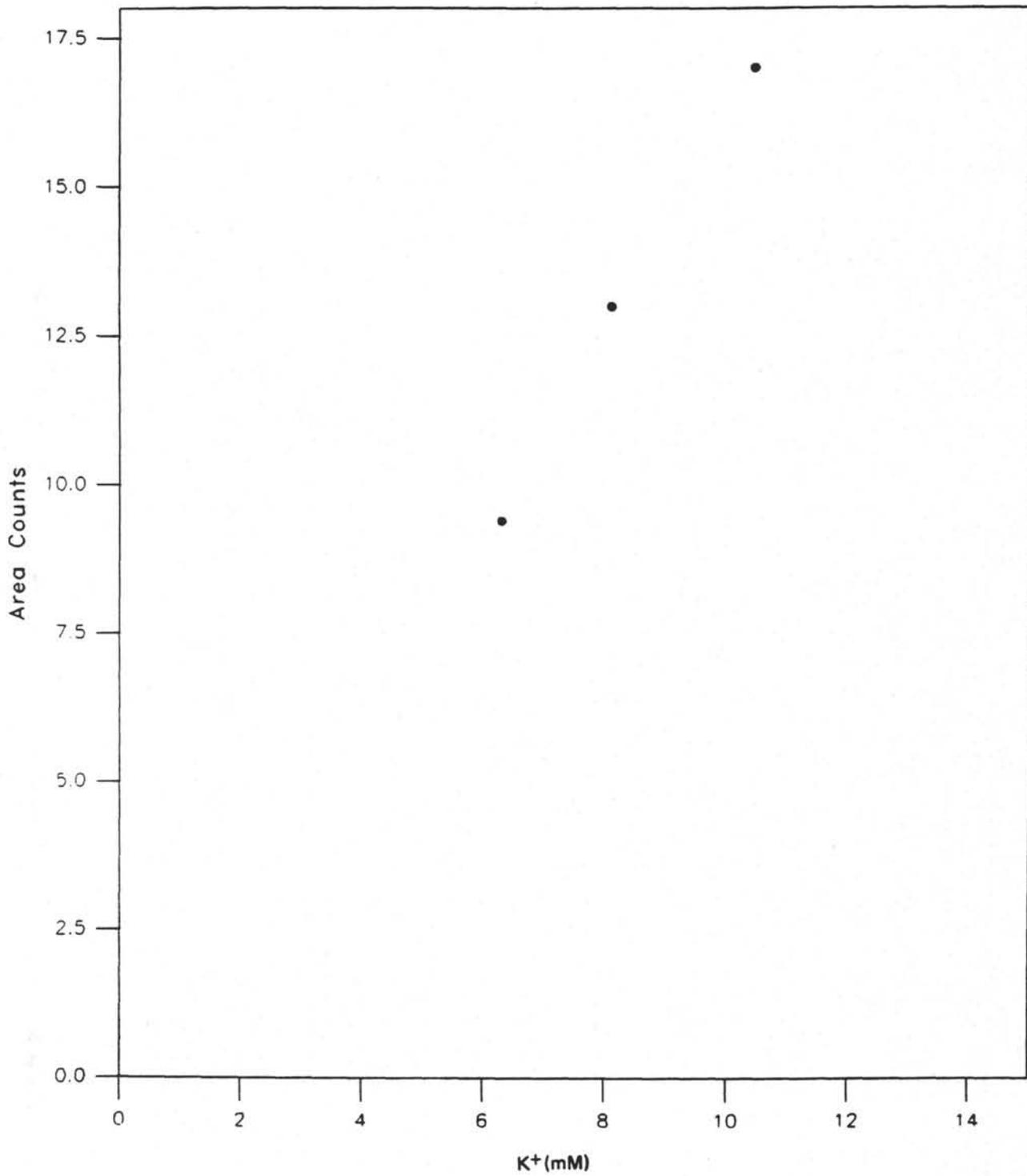


Figure 8. Potassium standard curve, from Dionex Ion Chromatograph analysis of Joris standards and IAPSO standard seawater.

5-cm³ glass vial. Add 1 cm³ deionized water to each, then 0.5 cm³ phenol alcohol solution, 0.5 cm³ sodium nitroprusside, and, finally, 1 cm³ oxidizing solution. Adding these solutions with Eppendorf pipettes is fast and convenient and insures proper mixing during addition. Shake samples after each addition. Standards should range from 0-1000 micromolar and should be treated like the samples above. Let the color develop for at least 1 hour and then determine the absorbance at 640 nanometers wavelength.

Some samples will have little color and may require aliquots larger than 0.1 cm³ sample (e.g., 0.5 cm³ sample, and standard). Many samples, however, may show excessively high absorbances and thus much smaller aliquots must be taken, e.g., as little as 0.005 cm³ or 0.01 cm³ for ammonia in case of concentrations of approximately 30 mM. Naturally, standards should cover the range of concentrations, or aliquots of standards can be adjusted to cover this range.

(2) Nitrite

(a) Introduction

Although generally there will be no need to determine nitrite in ODP samples, the method will be described below. This is justified because the nitrate method described in the following section uses the nitrite method after reduction of nitrate to nitrite.

The method given by Strickland and Parsons (1968) is used, modified for small samples. Good results have been obtained with the Gilford spectrophotometer, using the 1-cm cell.

In general, the nitrite is allowed to react with sulfanilamide in an acid solution. The resulting diazo compound reacts with N-(1-naphtyl)-ethylene diamine to form a pink azo dye which is measured at 543 nanometers.

(b) Reagents

Sulfanilamide solution: dissolve 5 g sulfanilamide in a mixture of 50 cm³ concentrated HCl (s.g., 1.18) and ca. 300 cm³ distilled water. Dilute to 500 cm³ with water. This solution is stable for many months.

N-(1-naphtyl)-ethylene diamine dihydrochloride solution: dissolve 0.50 g dihydrochloride in 500 cm³ distilled water. Store in dark bottle. The solution is not stable and should be renewed at least once a month or whenever a brown color develops.

(c) Procedure

To a 2-cm³ sample, add 0.1 ml sulfanilamide solution and allow to react for 2-8 minutes. Treat all samples in a similar manner. Then add 0.1 cm³ naphtyl ethylene diamine solution and mix immediately. After 10 minutes to 2 hours, measure on the spectrophotometer at 543 nanometers in 1-cm cell. Use distilled water as a blank.

(d) Standards

Dry sodium nitrite at 100°C for 1 hour. Dissolve 0.3450 g in 1000 cm³

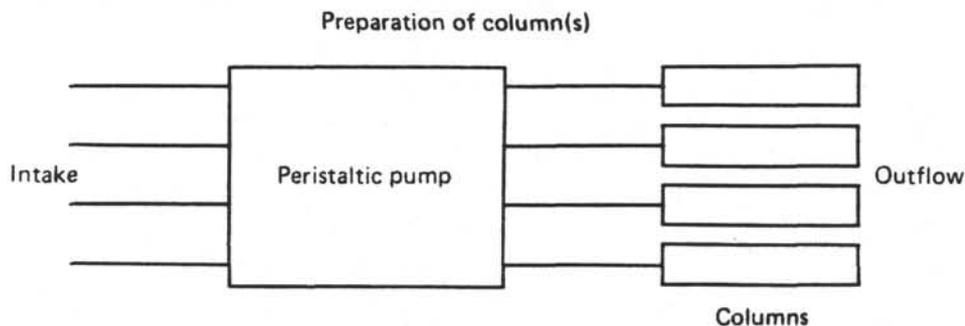
distilled water, Add 1 cm³ chloroform as a preservative: 1 cm³ = 5 micromoles N. Dilute 10 cm³ to 1000 cm³ with distilled water: 1 cm³ = 5 x 10⁻² micromoles N. Use same day. Now make standards covering the range between 0 and 5 micromoles/cm³.

3. Nitrate

(a) Introduction

Nitrate concentrations, especially in open ocean sediments with low accumulation rates, can be useful indicators of diagenetic processes involving organic carbon. For these reasons it will be useful to have this method available on board ship, even though the methodology is relatively laborious and will probably only be used when sampling programs are not busy. Concentration ranges will be between 0 and 60 uM. In areas where NH₄ concentrations rise rapidly, there will be no need to do nitrate determinations, as NO₃⁻ vanishes within a few meters from the sediment surface.

The method adopted from Strickland and Parsons (1968) makes use of the catalytic reduction of nitrite to nitrate, using a Cd-reduction column. A peristaltic pump is used to force the samples and standards through the reduction columns. Use of a one channel pump is preferred because it is simpler and less confusing. More columns can be used to save time; however, a standard curve must be produced for each column. Using multiple channels requires full attention in order to avoid mixing or contaminating solutions in the various channels.



Intake and outflow consist of 1/16" x 1/8" tygon tubing. Columns are 9 cm lengths of 3 mm teflon tubing. Put a small amount of glass wool in bottom of teflon tube (fine copper wool preferable). Fill about 5 cm length of tubing with small (0.5 to 2 mm) Cd chips. Put a small amount of glass or copper wool on top of packed column (one can put a small amount of copper turnings followed by glass wool on top).

Activation of Column(s)

If starting with new clean Cd, step 1 may be eliminated. (1) Pass 5% HCl through columns for a few minutes, then wash with water until effluent has neutral pH. (2) Pass 2% copper sulfate (CuSO₄·5H₂O) through columns for a few minutes (10-20 cm³) then wash columns with dilute NH₄Cl (see below).

(b) Reagents

Concentrated NH_4Cl : 175 g in 500 cm^3 H_2O . This solution is used for buffering samples and standards.

Dilute NH_4Cl : 50 cm^3 conc. NH_4Cl diluted to 2000 cm^3 . This solution is used for washing the columns.

Sulfanilamide and N-(1-naphthyl)-ethylene diamine dihydrochloride--see nitrite method.

(c) Procedure

If columns have not been used recently, it is advisable to run a few standards through them to check their activity.

Before running samples through the columns, pre-rinse them with dilute NH_4Cl .

Take 1 cm^3 sample or standard and add 4 cm^3 of low conductivity water.

Buffer samples and standards with conc. NH_4Cl : for a 5 cm^3 aliquot, use 0.1 cm^3 conc. NH_4Cl .

Run buffered samples through the columns--speed should be approximately $3\text{-}5 \text{ cm}^3/\text{minute}$. Collect the last 4 cm^3 . You will need 2 cm^3 for analysis (see nitrite method).

After all samples have been run through column, wash column with dilute NH_4Cl for several minutes.

To keep air out of system, immerse intake and outlet in water when not in use.

(d) Standards

Make standards from a stock solution of 10 mM KNO_3 . The range of standards should be from $0\text{-}60$ micromolar. Standards should be prepared in synthetic seawater: 30 g NaCl , $10 \text{ g MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.05 g NaHCO_3 in 1 dm^3 of H_2O .

(4) Silica

(a) Introduction

Determination of silica in pore waters of marine sediments depends upon (1) the production of a silicomolybdate complex and (2) the reduction of this complex to give a blue color. The present method (adapted from Strickland and Parsons, 1968) was described by Mann and Gieskes (1975).

(b) Reagents (Note: always use deionized, silica-free water)

Molybdate reagent: dissolve 4.0 ammonium paramolybdate -- $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (preferably fine crystalline) in ca. 300 cm^3 deionized water using a 500 cm^3 volumetric flask. Add 12 cm^3 concentrated hydrochloric acid (12N), mix, and make the volume to 500 cm^3 with deionized water. Store in a brown polyethylene

bottle out of direct sunlight. The reagent is stable for many months but should be discarded if any white precipitate forms. If unable to store properly, or if time permits, make fresh for each run.

Metol-sulfite solution: dissolve 6.0 g anhydrous sodium sulfite, Na_2SO_3 , in a 500-cm³ volumetric flask. Add 10 g metol (p-methylaminophenol sulfate) and then deionized water to make to 500 cm³. When the metol has dissolved, filter solution through a No. 1 Whatman filter paper and store in a clean glass bottle, preferably of dark glass, which is tightly stoppered. This solution, which may deteriorate quite rapidly and erratically, should be prepared fresh at least every month.

Oxalic acid solution: prepare a saturated oxalic acid solution by shaking 50 g analytical-grade reagent oxalic acid dihydrate (COOH)₂·2H₂O, with 500 cm³ deionized water. Let stand overnight. Decant solution from crystals for use. This solution may be stored in a glass bottle and is stable indefinitely.

Sulfuric acid solution 50% V/V: using a 500-cm³ volumetric flask, pour 250 cm³ concentrated analytical reagent-quality sulfuric acid into approximately 200 cm³ deionized water. Cool to room temperature and bring volume to 500 cm³ with a little extra water. Store in polyethylene bottle.

Reducing solution: mix 50 cm³ metol sulfite solution (#2) with 30 cm³ oxalic acid solution (#3). Add slowly, with mixing, 30 cm³ 50% sulfuric acid solution (#4) and bring volume to 150 cm³ with deionized water. Solution should be made daily, just before using. Multiply above amounts, depending on number of samples, using 3 cm³/sample.

Synthetic seawater: dissolve 25 g sodium chloride (NaCl) and 8 g magnesium sulfate heptahydrate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) in 1 dm³ deionized water and store in polyethylene bottle. The silica content of this solution should not exceed 1-2 micromoles-dm³.

(c) Standards

Silicate standard - sodium fluorosilicate: place a small quantity of Na_2SiF_6 in an open plastic vial and place in a vacuum desiccator overnight to remove excess water. Do not heat or fuse.

Primary standard: dissolve 0.5642 g Na_2SiF_6 in a 1-dm³ Nalgene volumetric flask. Dissolution is slow, so allow at least 30 minutes. This cannot be rushed. Use low conductivity water. The concentration of this standard is 3000 μM . Store in 500-ml polyethylene bottle. Standard is stable indefinitely.

Dilutions from primary standard: When making dilutions, use distilled water and store in polyethylene containers. Using a 50-cm³ volumetric flask, add the following amounts of primary and then bring to 50-cm³ total:

30 uM Si	-	0.5 cm ³ of primary
60		1
120		2
240		4
360		6
480		8
600		10
900		15
1200		20

Strickland and Parsons' (1968) preference for the sodium fluorosilicate over the silicic acid method is due to its long-term stability and ease of preparation.

(d) Method

Have all reagents prepared. Label and set up 3-dram plastic vials and caps (no pre-cleaning needed). Pour into vials 4.0 cm³ silica-free distilled water (3.8 cm³ for standards and blank). For standards and blank only, pipette in 0.2 cm³ synthetic seawater. Pipette 0.2 cm³ of sample or standard with Eppendorf pipette. Record time and immediately pipette 2.0 cm³ molybdate solution, using an Eppendorf pipette, into all vials. (The solution may also be titrated in.) Wait 15 minutes for yellow color to develop. Then add 3 cm³ reducing solution. Record time. Cap vials to reduce evaporation. Shake and wait 3 hours for blue color to develop. Read on Bausch and Lomb spectrophotometer at 812 nanometers, or on semiautomatic Gilford at 725 nanometers. Do not handle more than about 30 samples at a time.

There is no pronounced temperature effect if samples are run at room temperature (ca. 22°C).

The use of a Nalgene volumetric flask for the sodium fluorosilicate standard is suggested. The solution picks up silica rapidly from glass.

Do not use synthetic seawater in dilutions of the primary standard. This causes a decrease in the reactive silica content in a few hours, due to polymerization.

The 3-dram plastic vials and caps are convenient, cheap and disposable or easily washable.

The reason for adding the 0.2 cm^3 of synthetic seawater to the standards is to maintain a uniform salt content in relation to the samples.

Upon addition of molybdate to the sample, 15 minutes are allowed for the formation of the (yellow) complex. Tests have shown stability from 10 to 20 minutes. Whatever time is allotted should be consistent.

The time required for full formation of the blue color varies a little with the amount of silica being determined. After addition of reducing solution, it is suggested that 3 hours should pass before reading. Tests have shown stability of the blue complex is ca. 2-6 hours. Again, whatever time is allotted should be consistent.

(5) Phosphate

(a) Introduction

The phosphorous method is essentially the colorimetric one given by Strickland and Parsons (1968, p. 49), except that all reagents are made more dilute and small volumes are used. Basically, the method is that proposed by Presley (1971).

(b) Reagents

Ammonium molybdate solution: dissolve 2 g A.R. $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ in 1 dm^3 distilled water. Solution is stable indefinitely if stored in plastic bottle.

Sulfuric acid solution: dilute 10 cm^3 concentrated H_2SO_4 (specific gravity 1.82) to 1 dm^3 with distilled water.

Ascorbic acid solution: dissolve 3.5 g ascorbic acid in 1 dm^3 distilled water. Must be kept refrigerated and should not be stored for more than a week.

Potassium antimonyl-tartrate solution: dissolve 0.09 g $\text{KSbC}_4\text{H}_4\text{O}_7\cdot 1/2\text{H}_2\text{O}$ in 1 dm^3 distilled water. Solution is stable for many months.

Mixed reagent: mix together 50 cm^3 ammonium molybdate, 125 cm^3 sulfuric acid, 50 cm^3 ascorbic acid and 25 cm^3 potassium antimonyltartrate. Do not store this solution for more than a few hours.

Phosphate standard: dissolve 1.3614 g A.R. KH_2PO_4 in 1 dm^3 of water. This 0.01 molar phosphate (PO_4) standard is stable indefinitely unless biological growth develops.

(c) Procedure

Put 1.5 cm^3 of each sample and 1.5 cm^3 of a 5- μM , a 10- μM and a 20- μM phosphate (PO_4) standard (in distilled water) in 3-dram PVC vials. Do not make standards higher than 20 μM , as linearity breaks down above this level. Add 2 cm^3 of the mixed reagent. The resulting color, which develops in a few minutes and remains stable for several hours, is measured at 885 nanometers in 1-cm cells (or at 725 nanometers on the Gilford spectrophotometer).

Most of the DSDP samples analyzed have been below the detection limit of the technique (about 2 μM) since more than 1.5 cm^3 of sample is rarely available for analysis. However, the method will detect those waters that are significantly enriched in phosphate. Often dilutions are necessary, especially in near shore environments, where concentrations as high as 200 μM may occur.³ In such a case, standards should be prepared ranging up to 300 μM , and 0.1 cm^3 aliquots of samples and standards will do the job.

(6) Bromide

(a) Introduction

The bromide method is adapted from that described by Presley (1971).

(b) Stock solutions

0.05 M bromide: dissolve 2.975 g KBr in a 500 cm^3 volumetric flask and make to volume with distilled water. Shelf life is indefinite. This solution is used to prepare standards of concentrations between 0 and 50 micromolar.

Acetate buffer: dissolve 30 g NaAc in a 1 dm^3 volumetric flask. Add 7 cm^3 of glacial HAc and make to volume with distilled water. Shelf life is indefinite.

Phenol red: dissolve 16 mg phenolsulfonephthalein in a 100 cm^3 volumetric flask using 2 cm^3 of 0.1 N NaOH and make to volume with distilled water. Shelf life is indefinite.

(c) Freshly made solutions

0.005 N chloramine T: dissolve 0.28 g chloramine T in a 500 cm^3 volumetric flask and make to volume with distilled water. If stored in an amber bottle, shelf life is several weeks.

0.05 N sodium thiosulfate: dissolve 3 g of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in a 250 cm^3 volumetric flask and make to volume with distilled water.

Mixed reagent: pipette 25 cm^3 of phenol red stock solution into a 250 cm^3 volumetric flask and make to volume with acetate buffer stock solution.

(d) Standard solutions

Standards must range from 0-0.25 mM Br^- (the working range of the method). For these reasons, we make the following dilutions of the primary standard (described above as a stock solution):

0.5 cm^3 50 mM Br^- to 100 ml	0.25 mM
0.4	0.20
0.3	0.15
0.2	0.10
0.1	0.05

Pore waters usually range between 0-1 mM, and for these reasons we make a 5-time dilution.

(e) Procedure

- (1) Pipette 0.5 cm^3 of the standard solutions into a test tube (approx. 15 cm long).
- (2) Pipette 0.1 cm^3 sample (and also of IAPSO as a secondary standard) into a test tube and add 0.4 cm^3 low conductivity water.
- (3) Add 7.5 cm^3 mixed reagent to samples and standards.
- (4) Add 1 cm^3 chloramine T reagent. Mix for exactly 30 seconds with vortex mixer and add immediately afterwards 1 cm^3 sodium thiosulfate reagent and mix for another few seconds.
- (5) When all samples and standards are ready, measure absorbance at 595 nanometers.

Yield of the color complex is not proportional to (Br^-) but rather to a power of (Br^-) which depends on the strength of the reagents. A power fit to the standards yields satisfactory calibration curves.

(7) An Important Note of Caution

On Leg 92 we found out rather quickly that Whatman No. 1 filter paper contains nitrate in sufficient quantities to affect the nitrate data significantly. At that time, we washed all filter paper thoroughly in distilled water and dried it at about 60°C in the oven. The filter paper was then used in the pore water squeezing process without further deleterious effects. We recommend that this procedure becomes standard until nitrate-free paper (not acid-hardened!) is found.

IV. SAMPLING STRATEGIES

Often it is a good idea to follow calcium as the samples come in one by one from a drill hole. This will establish the direction of the Ca^{2+} concentration-depth gradient. There are three main types of gradients to be considered:

1. No change, or only very minor changes, with depth are observed. This usually means that other concentration changes, e.g., in Mg^{2+} and Cl^- will also be small and that the greatest accuracy is required during analysis of the water.

2. Ca^{2+} concentrations show an initial decrease with depth. This is often encountered in rapidly accumulating organic carbon rich sedimentation. Mg^{2+} concentrations can then show interesting patterns, e.g., maxima (c.f., Gieskes, 1983).

3. A definite increase in Ca^{2+} is observed. This is usually accompanied by fairly large decreases in Mg^{2+} .

Immediate analysis for Ca^{2+} provides the operator information enabling her/him to predict the behavior and concentrations of the other chemical components in the water. The fastest method to obtain this information is the colorimetric Ca_t titration described earlier.

The alkalinity titration should also be carried out as soon as possible. Remember to store the alkalinity sample after analysis in a plastic poly-tube with an indication of the total amount of acid added.

Often interstitial waters come in various amounts. It is, therefore, sensible to revise the sampling strategy for the Chemistry Lab aboard the JOIDES Resolution. This strategy is given in Table 8.

V. ACKNOWLEDGMENTS

It was a pleasure to be on the JOIDES Resolution in a modern chemistry laboratory. I (Gieskes) certainly appreciated the invitation to participate on Legs 102 and 110, and I hope that some of the above suggestions can be adopted.

Table 8. Sample distribution of interstitial waters.

- (1) If more than 20 cm³:
 - (a) Use 10 cm³ for alkalinity, storing in poly tube when done
 - (b) Store 2 x 5 cm³ in glass ampoules
 - (c) Use 5 cm³ for potential shipboard work
 - (d) Store remainder in poly tubes

- (2) If between 10 - 20 cm³:
 - (a) Use 5 cm³ for alkalinity, storing in poly tube when done
 - (b) Store 2 x 3 cm in glass ampoules
 - (c) Use 5 cm³ for shipboard work
 - (d) Store remainder in poly tubes and/or glass ampoules

- (3) If between 5 - 10 cm³:
 - (a) Omit alkalinity titration
 - (b) Store 2 x 2 cm³ in glass ampoules
 - (c) Use 2 - 3 cm³ for shipboard work
 - (d) Store remainder in poly tubes
Use sparingly: about 1 cm³ is needed for strontium analysis

- (4) If between 2 - 5 cm³:
 - (a) Omit alkalinity titration
 - (b) Store at least 1 cm³ in glass ampoule
 - (c) Use 1 cm³ for shipboard work; store in poly tube

- (5) If less than 2 cm³:

Put all in glass ampoule; do no shipboard analyses

Always keep squeezing until you really cannot get anything at all. A little water can still tell a big story!

VI. REFERENCES

- Bates, R.G. and Calais, J.G., 1981. Thermodynamics of the dissociation of Bis. H^+ in seawater from 5 to 40°C. J. Solution Chem., 10: 269-279.
- Bates, R.G. and Culberson, C.H., 1977. Hydrogen ions and the thermodynamic state of marine systems. In Anderson, N.R. and Malahoff, A. (Eds.), The Fate of Fossil Fuel CO_2 in the Oceans, New York and London (Plenum Press), 45-61.
- Carpenter, J. H. and Manella, M. E., 1973. Magnesium to chlorinity ratios in seawater. Limnol. Oceanogr., 78: 3621-3626.
- Culkin, F., 1965. The major constituents of seawater. In Riley, J. P. and Skirrow, G., (Eds.), Chemical Oceanography, 2: New York (Academic Press), 121-162.
- Gieskes, J.M., 1973. Interstitial water studies, Leg 15—Alkalinity, pH, Mg, Ca, PO_4 , and NH_3 . In Heezen, B.C., and MacGregor, I.D., et al., Init. Repts. DSDP, 20: Washington (U.S. Govt. Printing Office), 813-829.
- Gieskes, J.M., 1974. Interstitial water studies, Leg 25. In Simpson, E.S.W., and Schlich, R. et al., Init. Repts. DSDP, 25: Washington (U.S. Govt. Printing Office), 361-394.
- Gieskes, J.M., 1983. The chemistry of interstitial waters of deep sea sediments: interpretation of Deep Sea Drilling data. In Chemical Oceanography, 8: New York (Academic Press), 221-269.
- Gieskes, J.M. and Lawrence, J.R., 1976. Interstitial water studies, Leg 35. In Hollister, C.D., Craddock, C., et al., Init. Repts. DSDP, 35: Washington (U.S. Govt. Printing Office), 407-424.
- Khoo, K.H., Ramette, R.W., Culberson, C.H., and Bates, R.G., 1977. Determination of hydrogen ion concentrations in seawater from 5 to 40°C: standard potentials at salinities from 20 to 45 ‰. Anal. Chem., 49: 29-34.
- Mann, R. and Gieskes, J.M., 1975. Interstitial water studies, Leg 28. In Hayes, D.E., and Frakes, L.A., et al., Init. Repts. DSDP, 28: Washington (U.S. Govt. Printing Office), 805-814.
- McDuff, R.E., 1985. The chemistry of interstitial waters, Deep Sea Drilling Project Leg 86. In Heath, G.R., Burckle, L.H., et al., Init. Repts. DSDP, 86: Washington (U.S. Govt. Printing Office), 675-687.
- Presley, B.J., 1971. Techniques for analyzing interstitial water samples. part 1: determination of minor and major inorganic constituents. In Winterer, E.L., and Riedel, W.R., et al., Init. Repts. DSDP, 7, Pt. 2: Washington (U.S. Govt. Printing Office), 1749-1755.

- Salisbury, M.H., Scott, J.J., Auroux, C.A. et al., in press. Proc., Init. Repts. (Pt. A), ODP, 102.
- Solorzano, L., 1969. Determination of ammonia in natural waters by phenol-hypochlorite method. Limnol. Oceanogr., 14: 799-801.
- Strickland, J.D.H. and Parsons, T.R., 1968. A manual for seawater analysis. Bull. Fish. Res. Bd. Canada, 167: 311.
- Tsunogi, S., Nishimura, M. and Nakaya, S., 1968. Complexometric titration of calcium in the presence of large amounts of magnesium. Talanta, 15: 385-390.