APPENDIX: TECHNIQUES FOR ANALYZING INTERSTITIAL WATER SAMPLES

PART I: DETERMINATION OF SELECTED MINOR AND MAJOR INORGANIC CONSTITUENTS[1]

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Introduction

Most analyses of interstitial water must be done on small volume samples, because the amount of sediment available for water recovery is usually limited. This is especially true for the Deep Sea Drilling Project samples. During my work on these samples I have modified techniques in an attempt to obtain the maximum amount of data from the minimum amount of sample, while at the same time attempting to make the procedures as convenient and rapid as possible in order to facilitate handling of a large number of samples.

I am not convinced that my present techniques represent the ultimate in efficiency of sample use, or in speed and convenience, nor am I claiming any particular uniqueness or originality for most of the procedures. The procedures do, nevertheless, represent the current state of the art in our laboratory, and have evolved over a considerable length of time, and during the processing of a large number of samples. They are given here in order that our individual leg reports might be made more complete by reference to this section, for the convenience of new technicians who are taking over the routine work in our laboratory, and for the consideration of other investigators who might be faced with the problem of analyzing small samples. In general, the procedures represent rather minor modifications of published techniques, hence it seems pointless to go into great detail in describing them. I have tried, however, to include enough detail to allow the procedures to be successfully followed.

Three different types of water samples are normally received at UCLA from each leg of the Deep Sea Drilling Project. These are: Four samples of approximately 100 milliliters each, four of approximately 10 milliliters each, and a variable number, typically 15 to 50, of approximately 5 milliliters each. All water has been filtered through a 0.45-micron filter immediately after squeezing on the ship. The 10 and 100 milliliter samples are stored in polyethylene bottles. The 10 milliliter samples are frozen on board ship and are kept frozen until analysis is begun on shore. The 100 milliliter samples are kept refrigerated on shipboard and on shore, except for a few hours in shipment. The 5 milliliter samples are sealed in plastic syringes on board ship by pinching the heated tip closed and pouring RTV rubber around the syringe plunger. These samples are refrigerated in the same way as the 100 milliliter samples.

Experimental Procedures

Analyses of the 100 Milliliter Samples

The trace elements iron, cobalt, nickle and copper are determined on the 100 milliliter samples by solvent extraction and atomic absorption spectroscopy essentially as described by Brooks, *et al.,* (1967). Normally, one milliliter of the sample is first removed to use for the determination of chloride, manganese and zinc as described below. Next, a few drops of 6 N HCl is added to the sample in its original container to bring the pH down to 1 to 2. The sample is shaken, and allowed to sit overnight. This should bring any trace metal that might have precipitated back into solution. The pH is then adjusted to 3.5-4.0 by adding a few drops of 2 N NH$_4$OH.

The sample is poured into an acid-washed 100 milliliter graduated cylinder and the volume is recorded (the small dilution resulting from addition of acid and base can be ignored). If less than 100 milliliters of sample is available double distilled water is added to make the volume 100 milliliters. This is necessary in order to get the same recovery of the slightly soluble organic solvent from all samples and standards.

The 100 milliliter sample is poured into a 500 milliliter separating funnel and 10 milliliters of MIBK (methyl isobutyl ketone) are added, followed by 5 milliliters of a 1 per cent APDC (ammonium pyrollidine dithiocarbamate) solution. The samples are shaken vigorously for 3 minutes, and the phases separated. The aqueous phase is kept, because it can be used for sulfate or other major ion analyses. The organic phase is put into

a small acid-washed vial, then immediately transferred to a second acid washed vial. The small droplets of aqueous phase which inevitably contaminated the organic phase, and which interfere with analyses, are retained in the first vial by this procedure.

The organic phase is analyzed by atomic absorption spectrophotometry using standards prepared by spiking previously extracted surface seawater. The standards are extracted at the same time and in the same way as the samples are, thus compensating for incomplete extraction (Brooks *et al.*, 1967).

Analysis of 10 Milliliter Samples

The frozen samples were requested primarily for the purpose of analyzing for silicon and phosphate. It is commonly believed that the concentration of these constituents will change rapidly with storage if the sample is not frozen. However, this seems not to be the case for silicon, since our values for the Leg 4 samples agree reasonably well with those Manheim *et al.* determined on unfrozen samples. Further comparison will be made to see if, in fact, storage effects are negligible for the high silicon values commonly found in interstitial water.

Silicon is determined on the frozen samples essentially as outlined by Strickland and Parsons (1968) except that only one milliliter of sample and 25 milliliters of the molybdenum solutions are used (the molybdenum solution is diluted by a factor of 2.5 before use).

Phosphorus is determined by the reactive phosphorus method of Strickland and Parsons, except that only 2 milliliters of sample is used followed by approximately 25 milliliters of distilled water and 5 milliliters of the mixed reagent. The volume is then adjusted to 50 milliliters. More sample can be used when it is available, and in fact only an upper limit for PO_4 ($\approx$ 1ppm) has been obtained for most JOIDES samples using this combination of sample and final volume. This is, however, sufficient for determining whether or not a high enrichment of phosphate (PO_4) exists, such as that found by Brooks *et al.*, (1968).

Analysing the 5 Milliliter Samples

The syringes holding the 5 milliliter samples are taken from the refrigerator and the RTV rubber securing the plunger is removed by prying it out with a small screwdriver. The syringe and sample is then weighed on a torsion balance. The tip of the syringe is cut off with a scalpel, and all but about 1.5 milliliters of the water is injected into a reaction flask for total dissolved carbonate determination. The syringe is then reweighed to determine how much water has been transferred to the reaction flask. The water remaining

in the syringe is injected into a previously weighed snap cap plastic vial, and the vial and water is weighed to get the weight of water.

The snap cap plastic vials are very convenient for sample storage, but unless precautions are taken serious evaporation will occur within a matter of days. Screw-top polyethylene bottles are only slightly better in this respect. Our solution to this problem is to store all plastic vials and bottles in a tightly covered plastic box which contains a few tissues kept damp with seawater. The 100 per cent humidity inside the box effectively prevents evaporation.

The approximately 1.5 milliliters of sample in the plastic vial, which has been accurately weighed, is used for the determination of chloride, bromide, boron, manganese, zinc, lithium, strontium, sodium, magnesium, calcium and potassium, and usually silicon and NH_3. All analyses are done on dilutions made from the 1.5 milliliters of original sample. The complete procedure that I follow is described below.

The first dilution is accomplished by adding approximately 5 milliliters of double distilled water to the sample in its plastic vial. This is done using a Repipet® (Labindustries, Berkeley, California) set to 5 milliliters. The instrument is calibrated before and after diluting every group of samples by weighing water. A reproducibility of better than 0.2 per cent is easily obtained with this instrument, and a group of 20 to 30 samples can be diluted in a few minutes. After the first dilution there is approximately 6.5 milliliters of sample (the first dilution factor can be accurately calculated since both sample and dilutent weight are known). This 6.5 milliliters of sample is used for the various analyses as described below.

Chloride

The chloride determination is a titration with mercuric nitrate, essentially as given by Vogel (1961, p. 274).

Reagents

Indicator:
Make a 0.2 per cent solution of diphenylcarbohydrazide in ethyl alcohol. Diphenylcarbozone is the recommended indicator, but the carbohydrazide has been found to work well, probably because it oxidizes to the carbozone.

Mercuric Nitrate, $\approx$ 0.1 N:
Accurately weigh about 10.0 grams of pure mercury and add it to a 50 milliliter Erlenmeyer flask containing 25 milliliters of water. Heat on a hot plate and slowly add concentrated nitric acid until all the mercury dissolves. Boil to drive off nitrous fumes, cool,

and 2 milliliters of concentrated nitric acid, and make up to one liter with distilled water.

Calculate the exact normality from the weight of mercury used, and dilute an aliquot to 0.02 N with distilled water for use. The concentration should be checked by titration against diluted standard seawater, but should be very close to that calculated.

Procedure

One milliliter of the first dilution is removed from the plastic vial with a 1000 lambda Eppendorf pipet (Curtin Scientific, Santa Fe Springs, California). This automatic syringe-type device is convenient, rapid, and is similar in reproducibility to an analytical pipet. The one-milliliter aliquot is injected into a clean 10 milliliter glass vial, and 6 or 8 drops of the indicator solution are added. A small magnetic stirring bar is dropped in and the solution is stirred as the 0.02 N mercuric nitrate is added from a 10 milliliter burette.

An intense purple color will start developing in the clear solution long before the end point is reached, and will fade more and more slowly as the end point is approached. At the end point the entire solution will assume a slightly pinkish-purple tinge, and 1 or 2 additional drops of mercuric nitrate will give a persistent intense purple color. As with any indicator, the end point is subjective, and each worker should establish his own using standard seawater diluted by a factor of four.

I have found this procedure to be as reproducible as most potentiometric titration procedures, and it is much more rapid and convenient. The standard deviation on replicate analyses of standard seawater is 0.1 per mille, and while this would not be acceptable for most oceanographic work, it is quite adequate to show any significant change in interstitial water chemistry.

Bromide

The bromide procedure is modified from an unpublished one used by G. Baker of Chevron Oil Field Research Company, and was originally proposed by Baltre (1936). It envolves oxidizing the bromide with chloramine-T in the presence of phenol red and acetate buffer, and measuring the resulting color spectrophotometrically at 595 millimicrons.

Reagents

Bromide Standard:
Dissolve exactly 0.3723 grams of dry reagent grade potassium-bromide in 500 milliliters of distilled water. This 500 ppm stock solution is diluted for use.

Chloramine-T Solution:
Dissolve 2.8 grams of chloramine-T salt (sodium paratoluene-sulfonchloramine, Eastman No. 1022) in 500 milliliters of distilled water. This will be about 0.5 N in oxidizing strength. If stored in an amber bottle, the solution is stable for several weeks. The solution can be standardized before use by potentiometric titration against standard thiosulfate, but if a new working curve is prepared from bromide standards for each new group of samples, this is not necessary. The 0.05 N stock solution is diluted to 0.005 N just prior to use.

Acetate Buffer:
Dissolve 30 grams of sodium acetate ($NaC_2H_3O_2 \cdot 3H_2O$) in about 500 milliliters of distilled water. Add 7 milliliters of glacial acetic acid and dilute to one liter.

Phenol Red:
Dissolve 16 mg of phenolsulfonephthalein (Eastman #541) in 2 milliliters of 0.1 N NaOH and dilute to 100 milliliters with distilled water.

Sodium Thiosulfate:
Dissolve 1.5 grams $Na_2S_2O_3 \cdot 5H_2O$ in 250 milliliters of distilled water. This will be about 0.05 N, but the exact normality is not important. It is important, however, to make fresh reagent every few days because the solution is unstable.

Mixed Phenol Red-Acetate Buffer:
Pipette 25 milliliters of phenol red into a 500 milliliter volumetric flask and make it up to the mark with acetate buffer.

Procedure

Use an Eppendorf pipette to transfer 1 milliliter of the first sample dilution to a clean 50 milliliter Erlenmyer flask. Add mixed phenol red-acetate buffer from a Labindustries Repipet, set to 15 milliliters (the exact volume is not important, but must be constant). One milliliter of a 10, a 15, and a 20 ppm bromide standard should be similarly treated, and 1 milliliter of standard seawater by 0.25 can be used as a check on the prepared standards.

The next step in the procedure is time-critical and all reagents and equipment must be ready for instant use.

Set a Repipet filled with 0.005 N chloramine-T to 2 milliliters. Slowly raise the plunger to the stop and hold it there with one hand. With the other hand, start a stopwatch running, then quickly pick up one of the Erlenmyers containing sample or standard plus phenol red-acetate buffer. Inject the 2 milliliters of chloramine-T into the Erlenmeyer and immediately start swirling the contents. This swirling is to continue for exactly 30 seconds. While swirling the Erlenmeyer with one hand, with the other hand raise the piston of a Repipet filled with 0.05 N sodium thiosulfate and set to 5 milliliters. At the end of 30 seconds, inject the

thiosulfate into the Erlenmeyer. Continue the swirling for an additional 10 seconds, set the solution aside, and get ready for the next sample.

When all samples and standards have been processed, transfer them to one-inch cells and measure the color intensity at 595 millimicrons against a reagent blank processed in the same manner.

Make a working curve by plotting concentrations of standards against absorbency. If the procedure is followed closely, every point will be almost exactly on a straight line, however the line will not go through zero. This has not been a problem in my work, because all samples are always bracketed by the standards, hence the sample concentrations can accurately be read off the working curve.

The standard deviation of replicate analyses of standard sea water diluted by four is 0.5 ppm.

Sodium, Magnesium, Calcium and Potassium

The four major cations are determined by atomic absorption or flame emission spectroscopy using 0.5 milliliter of the first dilution in the following way:

A second dilution is made with an approximately 5000 ppm lanthanum solution made from $LaCl_3$ or from La_2O_3 dissolved in 0.5 N HCl. The exact strength of lanthanum and acid is not important, but it is essential that the same solution be used to dilute all samples and standards, and that it be used as a blank in the analysis. The impurities in lanthanum compounds have been found to vary from batch to batch and each new batch must be analyzed before it is used to dilute samples. If it gives a signal more than a few percentage of that to be expected from the samples it should be rejected and a different batch tried.

The lanthanum solution is put into a Repipet set to 10 milliliters, and at least three aliquots of the solution are weighed to determine the exact weight of solution being delivered. After the dilution is completed at least three more aliquots are weighed as a check. Reasonable care with the Repipet will give a standard deviation of less than 0.01 gram, hence a negligible error.

The sample, 0.5 milliliter of the first dilution, is put into a 5-dram PVC snap cap vial with a 500 lambda Eppendorf pipette, then the lanthanum solution is added. I calibrate the pipette by weighing 8 or 10 aliquots of standard sea water diluted 1 to 4. The standard deviation from the mean weight added can be kept to 0.0005 gram if extreme care is taken in using the Eppendorf pipette, but larger errors will result unless the addition is done carefully. This second dilution, like the first, is figured on a weight/weight basis, because the sample densities vary insignificantly from that of the diluted standard seawater.

A third dilution is made in a manner analogous to the second. A Repipet is filled with double distilled water, set to deliver 16 milliliters, and calibrated by weighing. The 500 lambda Eppendorf pipette is calibrated by weighing standard seawater diluted 80 to 1. One-half milliliter of the second dilution is put into a 5-dram vial and 16 milliliters of double distilled water is added. Again the dilution factor is figured on a weight/weight basis.

The second dilution is used to determine calcium and potassium by atomic absorption spectroscopy, using the instrumental parameters suggested by the manufacturer (Perkin-Elmer Corp.), and a working curve made from standards in the lanthanum solution used to dilute the samples.

I also weigh out three different aliquots of standard seawater and carry them through the entire dilution and analysis procedure along with the samples. The concentration of the major cations in these samples can be calculated from the chlorinity and the dilution factor, and should fall on the line drawn for the standards, if no errors have been made in the procedure.

Magnesium is determined on the third dilution by atomic absorption spectroscopy, again using the instrumental parameters suggested by the manufacturer and standards prepared in the matrix used to dilute the samples. Sodium can be similarly determined, but due to the instability of the Sodium lamps I prefer to use the flame emission accessory on the atomic absorption spectrophotometer. The air-acetylene flame excites enough sodium atoms to provide a strong signal. I do the flame emission analysis in the following way:

Set the wavelength indicator to 5890 Å and the slit width to 3. With the flame emission accessory and the external chopper on, and with the instrument aspirating the most concentrated standard, slowly move the wavelength dial to obtain maximum signal. It will be necessary to adjust the gain setting at the same time so as to obtain a signal approximately 75 per cent of full scale. The burner height and position should also be adjusted so as to maximize the signal, thus allowing a lower gain setting and a more stable reading.

Make a working curve by plotting chart units against concentration of standards. It is essential to have standards both more and less concentrated than the samples, because the working curve may be linear over a relatively narrow range, for example 2.5 to 4.5 ppm. Diluted standard seawater can be used as a check on the standards, but is probably itself the best primary standard. I have found those commercial standards which are stored in polyethylene bottles give erroneous results, probably because they become concentrated due to evaporation through the container walls.

I have found the following standard deviations for replicate analyses of diluted standard seawater (after multiplication by the appropriate dilution factor): sodium–0.2 g/Kg; magnesium–20 mg/Kg; calcium and potassium–10 mg/Kg.

Lithium

Lithium is determined by air-acetylene flame emission analysis in a manner analagous to that for sodium. The instrument parameters used in work reported to date (6708 Å, slit width 4) gave a working curve which flattened sharply at about 45 ppb, which caused problems in many cases because interstitial waters are often greatly enriched in lithium. My solution to this problem was to further dilute the first sample dilution to insure that all samples contain less than 45 ppb lithium. This too can lead to error, however, because the samples and standards then contain variable amounts of sodium and other interfering ions. The problem of non-linear working curves and many interference problems can be solved by using a narrower slit and a higher gain setting. This introduces considerably more noise into the signal, but gives reliable data.

The lithium dilution is accomplished by transferring 0.5 milliliter of the first dilution to a 3-dram PVC vial using a 500 lambda Eppendorf pipette, then adding 2 milliliters of double distilled water with a 1000 lambda Eppendorf pipette. The solution is swirled gently to insure mixing, then 1 milliliter is removed and placed in another 3-dram plastic vial. This 1 milliliter is aspirated into the atomic absorption spectrophotometer for flame emission analysis of lithium.

It is difficult to make a proper standard and blank for the lithium determination, because most artificial seawater mixtures contain almost as much lithium as the samples do. I have analyzed seawater from several localities in the Pacific ocean, as well as I.A.O.P. standard seawater, and find that all these waters give essentially the same signal for lithium. Hence, my practice has been to use diluted seawater as a standard for lithium. The standard deviation of replicate analysis of standard seawater is 10 ppb.

Silicon

The silicon determination is made on the water remaining in the plastic vials after removal of the lithium sample. One and one-half milliliters standard silicon solutions of 0.25, 0.5, 1.0 and 2.0 ppm silicon are added to 3-dram PVC vials, and are used to make a working curve.

The method is a colorimetric one, essentially as given by Strickland and Parsons (1968) except for the small sample and reagent volumes used in the present method.

Add 1 milliliter of molybdenum solution (Strickland and Parsons) to the 1.5 milliliters of sample or standard in the PVC vial, cap, and let sit. After 10 minutes add 1 milliliter of reducing solution (Strickland and Parsons) and let the color develop for 1 hour. Transfer the solutions to 1-centimeter cells and measure the color intensity at 8100 Å. The working curve of absorbency against concentration should be a straight line going through zero.

The standard deviation of replicate analyses of a 0.5 ppm silicon standard is estimated to be 0.025 ppm.

Ammonia

Ammonia is determined colorimetrically by a slight modification of the method of Solorzano (1969).

Reagents

Phenol-Alcohol Solution:
Dissolve 0.8 gram of reagent grade phenol in 100 milliliters of 95 per cent ethyl alcohol.

Sodium Nitroprusside Solution:
Dissolve 0.15 gram of sodium nitroprusside (sodium nitroferricyanide) in 200 milliliters of deionized water. Store in an amber bottle for not more than a month.

Alkaline Solution:
Dissolve 7.5 grams of trisodium citrate and 0.4 gram of NaOH in 500 milliliters of deionized water.

Oxidizing Solution:
Add 2 milliliters of fresh sodium hypochlorite (5 per cent available chloride) to 100 milliliters of the alkaline solution and use the same day.

Ammonia Standard:
Dissolve 3.141 grams of A. R. ammonium chloride, dried overnight at 100°C, in 1 liter of deionized water. This is a 1000 ppm (mg/1) NH_3 stock solution, and is diluted with deionized water for use.

Procedure

Use a 500 lambda Eppendorf pipette to transfer 0.5 milliliter of each first sample dilution to a 3-dram PVC vial (some samples will have to be diluted further and rerun, but some will give no color at this dilution). Also put 0.5 milliliter of 0.25, 0.50, 1.0 and 2.0 ppm ammonia standards into vials. Add 1 milliliter of deionized water to each, then 0.5 milliliter of the phenol alcohol solution, 0.5 milliliter of sodium nitroprusside and, finally 1 milliliter of oxidizing solution. Adding these solutions with Eppendorf pipettes is fast and convenient and it insures proper mixing during addition.

Allow the color to develop for one hour, transfer to 1 centimeter cells, and measure the intensity at 6400 Å against a reagent blank. The working curve of absorbency versus concentration should be a straight line going through zero. The standard deviation for replicate analyses of a 0.5 ppm standard is estimated to be 0.025 ppm.

Phosphorus

The phosphorus method is essentially the colorimetric one given by Strickland and Parsons (1968, page 49) except that all reagents are made more dilute and small volumes are used.

Reagents

Ammonium Molybdate Solution:
Dissolve 2 grams of A.R. $(NH_4)_6MO_7O_{24} \cdot 4H_2O$ in 1 liter of distilled water. The solution is stable indefinitely if stored in a plastic bottle.

Sulphuric Acid Solution:
Dilute 10 milliliters of concentrated H_2SO_4 (specific gravity 1.82) to 1 liter with distilled water.

Ascorbic Acid Solution:
Dissolve 3.5 grams of ascorbic acid (this reagent must be kept refrigerated) in 1 liter of distilled water. The solution should not be stored for more than a week.

Potassium Antimonyl-Tartrate Solution:
Dissolve 0.09 gram of $KSbC_4H_4O_7 \cdot \frac{1}{2}H_2O$ in 1 liter of distilled water. The solution is stable for many months.

Mixed Reagent

Mix together 50 milliliters ammonium molybdate, 125 milliliters sulphuric acid, 50 milliliters ascorbic acid and 25 milliliters potassium antimoryl-tartrate. Do not store this solution for more than a few hours.

Phosphate Standard:

Dissolve 1.433 grams of A.R. KH_2PO_4 in 1 liter of water. This 1000 ppm (mg/1) phosphate (PO_4) standard is stable indefinitely unless biological growth develops.

Procedure

Put 1.5 milliliters of each sample (first dilution) and 1.5 milliliters of a 0.5, a 1.0, and a 2.0 ppm phosphate (PO_4) standard (in distilled water) in 3-dram PVC vials. Add 2 milliliters of the mixed reagent. The resulting color, which develops in a few minutes and is stable for several hours, is measured at 8850 Å in 1-centimeter cells.

Most of the Deep Sea Drilling Project samples analyzed have proven to be below the detection limit of the technique as described (about 0.25 ppm) but seldom is more than 1.5 milliliters of sample available for analysis. The method will, however, detect those waters which are significantly enriched in phosphate (PO_4).

The standard deviation of replicate analyses of a 0.5 ppm standard is estimated to be 0.025 ppm.

Boron

The boron method is modified from a colorimetric one described by Grinstead (1967).

Reagents

Ammonium Acetate-Acetic Acid Mixed Solution:
Solution:
Dissolve a one-pound bottle of A.R. $NH_4C_2H_3O_2$ in distilled water and dilute to 2 liters (this reagent is so deliquescent it is difficult to weigh, it is more convenient, therefore, to use an entire bottle). Before use, add 1 part glacial acetic acid to 3 parts of the ammonium acetate solution.

Curcumin Solution:
Make a 0.2 per cent solution of curcumin (Eastman #1179) in glacial acetic acid, warming if necessary to complete the dissolution.

Sulphuric Acid—Acetic Acid Mixture:
Add slowly and while stirring 500 milliliters of concentrated sulphuric acid to 500 milliliters of glacial acetic acid.

Boron Standard:
Dissolve 5.715 grams of dry A.R. boric acid in 1 liter of distilled water. This makes a 1000 ppm (mg/1) stock solution.

Artificial Seawater:
Make an artificial seawater that is similar to the samples in total dissolved solids by dissolving 7.5 grams of A.R. NaCl and 1.2 grams of A.R. $MgSO_4$ in 1 liter of distilled water. Use this artificial seawater to make a reagent blank and for making standards from the stock boron solution.

Procedure

Put 0.5 milliliter of each first sample dilution, 0.5 milliliter of the artificial seawater, and 0.5 milliliter of 0.5, 1.0 and 2.0 ppm boron standards into well cleaned (no borax!) 50-milliliter plastic bottles. Add 2 milliliters of curcumin solution, swirl to mix, then add 2 milliliters of mixed sulphuric-acetic acid (these solutions are difficult to handle with conventional pipettes,

but can be added quickly and easily with Repipets). Swirl to completely mix the viscous solutions and allow them to sit for 30 minutes. Add 20 milliliters of the ammonium acetate-acetic acid solution and mix well. Transfer to 1-inch cells and measure the color intensity at 5550 Å.

A working curve of concentration in standards versus absorbency should be a straight line going through zero. Surface seawater diluted by factors of 3, 4 and 5 can also be used in the procedure and should give concentrations very close to the expected values.

The standard deviation of replicate analyses of surface sea water diluted by 4 is 0.05 ppm.

Manganese and Zinc

Manganese and zinc can be determined by direct aspiration of the first sample dilution into an atomic absorption spectrophotometer equipped with a Boling burner head. In general, the instrumental parameters recommended by the manufacturer (Perkin-Elmer Corp.) are followed, and the signal is recorded by a Sargent recorder.

Standards are prepared by spiking filtered open ocean water diluted 1 to 4, which is also used as a blank, because the manganese and zinc content of this water is negligible compared to that in many interstitial waters.

The detection limit of this method is approximately 20 ppb, and the standard deviation at 200 ppb is estimated to be 10 ppb.

Sulfate

Sulfate is determined gravimetrically on water that has been used for total dissolved carbonate determination (the carbonate procedure is described in a separate section). The water is transferred from the carbonate reaction flask to a 150 milliliter beaker by repeated washing, giving a final volume of approximately 75 milliliters.

The solutions are heated to incipient boiling on a hot plate, then 5 milliliters of a 10 per cent (w/v) $BaCl_2$ solution is slowly added while the solution is stirred. The hot plate is turned off and the solutions are allowed to slowly cool. They are left overnight to complete the precipitation of barium sulfate ($BaSO_4$).

The next day approximately 50 milliliters of the clear solution is decanted off and the remainder is filtered through a previously weighed 25-millimeter diameter, 0.45-micron pore size membrane filter. The filter holding the barium sulfate ($BaSO_4$) is dried overnight at 100°C, cooled in a desiccator, and weighed.

The empty filters normally weigh about 30 milligrams, and those from a given package will vary in weight by less than 1 milligram, nevertheless each is weighed separately and the weight is recorded for use in calculating the weight of barium sulfate ($BaSO_4$), because this can be a small number for some samples. It has been found that the filters lose about 0.5 milligram weight on drying at 100°C, so this value is subtracted from the filter weight.

After weighing, the filters holding the barium sulfate ($BaSO_4$) are put into small plastic vials for later sulfur isotope work.

The standard deviation of replicate analyses of 4-milliliter samples of surface seawater is 0.3 milligrams sulfate (SO_4).

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