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"Research and Evaluation of Trace Element  
Methodology for the Analysis of Sea Water"

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## Introduction

The literature of marine water analysis reflects the considerable difficulty in establishing an accurate and precise method of analysis for trace metals. Conflicting reports of the average concentrations of metals show that the complex matrix defies a simplified approach. For example, specific sampling techniques, container" contamination differences in salinity, suspended particulate matter, and analytical technique have to be considered. In the past decade analytical instrumentation and techniques have been developed to vastly improve the precision of the analytical measurement. However, little attention has been paid to the problem of sampling and storage of the sample prior to chemical analysis. The solving of the analytical analysis problem is of little use until a representative sample can be taken, free of contamination, and properly stored until analysis.

It is important to remember that trace elements in sea water have three very closely related interfaces with its environment : the atmosphere, the lithosphere, and the biosphere [1]. Each of these areas are actively involved and each has special properties which can drastically effect the metal content of the sea. Therefore, it is no wonder that much of the early analytical data is unreliable [2].

Components of sea water can be conveniently divided into two groups: major components (present in quantities greater than 1 mg/l) and minor components (present in quantities less than 1 mg/l). Major components are present in the same proportions throughout the oceans of the world, whereas minor components vary with locality, depth, etc. The average composition of sea water has been tabulated by Goldberg [3] and more recently by Segar and Cantillo [4] . As can be seen from reviewing these and other data in the

literature of individual elements, considerable variations have been reported. This is due in part to variations in different parts of the ocean and at different times; although some of the variation is due to the differences in analytical methods used to analyze the samples. In general, it is agreed by most workers that contamination plays a major role.

This report does not attempt to answer questions regarding the accuracy of sampling or even of subsequent contamination of the samples during storage. By the method of sample splits and exchange of samples between laboratories it should be possible to demonstrate whether or not the actual analytical methods being used are reliable. For this purpose, the choice of samples to be analyzed is not too important. While attempts have been made to minimize sampling or contamination errors, it is recognized that these samples are far from ideal and probably will give only a fair estimate of the true trace element content in Alaskan waters.

#### Separation

Most of the trace metals listed as minor components cannot be determined by conventional analytical methods (flame atomic absorption spectrometry (AAS), polarography, or calorimetry) without a separation and/or preconcentration step. The most common concentration techniques are coprecipitation, electrolysis, solvent extraction and ion-exchange resins. Coprecipitation has the disadvantages of being a lengthy process and of requiring the removal of the precipitation ion. Burrell [5] and Chau et al. [6] coprecipitated trace elements in sea water with ferric hydroxide, followed by chelation and solvent extraction to remove the iron. The procedure was tedious and it was necessary to apply large blank corrections. Sato and Saitoh [7] coprecipitated chromium from a liter of sea water with zirconium

hydroxide. The zirconium hydroxide was removed by filtration and then dissolved in 2N hydrochloric acid. The analysis was by AAS using a carbon furnace. Feldman and Rains [8] used sodium tetraphenylboron to separate cesium and rubidium from five liters of sea water and then completed the analysis by flame emission spectrometry.

For the analysis of cadmium, lead, and zinc in sea water the elements were electrolyzed on a hanging mercury drop electrode [9]. The mercury was washed and then transferred to a graphite boat. The mercury was vaporized at 440 °C, the metals atomized at 1700 °C and determined by AAS. Some problems encountered were losses of analyte during electrolysis in which the electrolysis cell had to be coated with silicon. A disadvantage of the technique is that only certain elements can be separated and only a fraction of the analyte is electrolyzed which reduces the sensitivity of the method. In a variation Lund and Larsen [10] electrodeposited cadmium on a tungsten filament which was then heated electrically and the cadmium determined by AAS.

The chelation of metals with organic ligands and subsequent extraction into various solvents has long been used as an analytical technique. Table 1 lists several organic ligands used to preconcentrate trace elements in sea water. It is well known that ammonium pyrrolidine dithiocarbamate (APDC) is a useful chelating agent for a number of transition metals [11-15]. Gilbert and Clay [16] extracted Cr (VI) from 800 ml of sea water with APDC-MIBK (methyl isobutyl ketone) and then determined the chromium by AAS. The chromium is oxidized with permanganate in a 50 °C hot water bath, the sample is acidified to pH 2, cooled, and then the chromium APDC complex extracted into MIBK. A major difficulty of preconcentration with APDC-MIBK is the effect of the aqueous ( $V_a$ )/organic ( $V_o$ ) phase ratio [13]. The degree of extraction

decreases as the ratio of  $V_a/V_o$  increases. To overcome this times. Also, the volatility of the organic solvent in sea water is a critical factor. Table 2 gives of volatility of the most frequently used solvents in water. To alleviate this difficulty, mixed solvents have been used [8]. By using a 3:1 mixture of MIBK-cyclohexane the volatility of MIBK is decreased without changing the extraction coefficient or the subsequent burning characteristics of the ketone.

Ordinary ion exchange resins are of limited use in the concentration of elements from strong electrolytes, such as sea water because the level of major ions (Na, Mg, Ca, and K) requires the use of very high capacity columns thus raising the column blank to unacceptably high levels. Chelating resins can be very useful for this separation of the matrix ions since these are not chelated by the resin. Muzzarelli and Rocchetti [18] used chitosan (a natural" chelating polymer) to separate vanadium from the alkali and alkaline-earth salts in sea water. After passing a liter of sea water through the column, the chitosan is removed, washed with ethanol and dried. Then, 5 mg test portions of the solids are inserted into the graphite furnace and vanadium determined by AAS. The maximum recovery was however 80 percent for 1.6  $\mu\text{g}$  of vanadium in 100ml of three percent sodium chloride solution and in the presence of sulfuric acid the efficiency of the column dropped to 55 percent.

Lai et al. [19,20] found that between 20 and 50 liters of sea water could be passed through a single small column of Chelex 100 with complete retention of Ag, Co, Fe, Pb, and Zn.

Riley and Taylor [21] used Chelex 100 to collect the heavy metals from a liter of sea water and found quantitative (>99%) retention and elution for Bi, Cd, Ce, Co, Cu, In, Pb, Mn, Ni, Sc, Th, V, Y, and Zn.

Kingston [22] found quantitative recovery of Cu, Fe, Mn, Ni, and Zn from four liters of sea water at a flow rate of 33 ml per minute. The collection of ions was done between pH 5.0 and 5.5 uniformly for all the elements of interest with hydrochloric acid used as the elutant. The final analysis was completed by flame AAS.

Davey and Soper [23,24] have constructed a Chelex 100 *in situ* column sampler and have found, of the ions tested,  $^{65}\text{Zn}$ ,  $^{115\text{m}}\text{Cd}$ ,  $^{54}\text{Mn}$ ,  $^{64}\text{Cu}$  were retained at  $\geq 99$  percent, while  $^{210}\text{Pb}$ ,  $^{63}\text{Ni}$ , and  $^{59}\text{Fe}$  were retained at 92-95 percent. These results were obtained however using the natural pH of sea water ( $\sim 8.1$ ) which is higher than suggested by other researchers for this separation,

## Experimental

### Sampling, Storage, and Contamination Control

There are nearly as many methods of sampling as there are investigators and virtually all methods contain some deficiencies. However, it is not the purpose of this project to resolve sampling problems, but rather to investigate analytical differences between sample splits of an arbitrary group of samples. Although the method and type of sample taken for this experiment are immaterial, a few comments are made about the NBS sampler.

The sampler used was that developed by Harrison et al. [25] and is unique in its design and method of construction. While there are, unavoidably, a few metal parts, these are made entirely of aluminum and have been double coated with a very tough, thick coating of Teflon FEP fluorocarbon resin. The rest of the sampler is constructed from a block of virgin Teflon TFE. The only remaining parts are nylon

(nuts, bolts, and washers) and nylon rope to raise, lower, open and close the sampler. An integral attachment machined from Teflon TFE is designed to permit on site filtering of the sample through a 47 mm Nuclepore 0.4 micron membrane filter. For reference, further details are reproduced in Appendix I.

A common deficiency of many samplers is the inappropriate selection of materials used in the sampler which unavoidably cause contamination of the sample. The NBS sampler was designed specifically for very low contamination levels. Before transporting to Alaska for taking samples, the NBS samplers were completely disassembled and cleaned in acid. These parts were stored in clean polyethylene bags to be re-assembled on the sampling site in Alaska. Metal parts whose Teflon coating was scratched or damaged were replaced with parts having new or intact coatings.

Another common cause of contamination is in the selection and cleaning of bottles for sample storage. Maienthal and Becker [26] have reviewed the literature on the handling and storage of liquid and solid samples. Moody and Lindstrom [27] have investigated the applicability of commercially available bottles to the storage of liquid samples. The least contaminating bottles were found to be bottles constructed of Teflon and polyethylene, respectively. Methods were also developed to assure adequate cleaning of these bottles.

For the NBS sampling trip to Alaska, 40 one-liter Teflon FEP bottles were subjected to very rigorous cleaning [28]. Half of these bottles were then filled with the highest purity distilled water. To the remaining 20 clean Teflon bottles 44 g of ultra high purity  $\text{HNO}_3$  was added for the purposes of acidifying a one-liter sea water sample to 0.5N with  $\text{HNO}_3$ . The acid and water used at these stages represent one of the few remaining chances for contamination of the sample. Even

though the acid is of the highest attainable purity, a glance at the impurity levels will still reveal the need to make a correction for some elements for contamination due to the acid blank. Further details about reagents used are reproduced in Appendix II.

The NOAA ship *Surveyor* was used to transport men and equipment from Juneau to the selected sample site, Glacier Bay, Alaska . The original NBS plans were to sample four different ways. Half of the samples were to have been filtered through 0.4 micron Nuclepore filters and the rest were to have been unfiltered. Half of each of these samples were to have been acidified and half were to have been unacidified. Thus the sample classification would have been filtered (acidified and non-acidified) and unfiltered (acidified and non-acidified) .

Unfortunately, once on board, it was learned that the sampling time allocated to NBS was far less than was needed to complete the project. Using the 0.4  $\mu$  filter and two samplers, it was possible to filter about 500 ml every 15-20 minutes . The total time allocation for inorganic sampling was less than one hour, much of which was lost trying to set up and clean the sampler and filter apparatus. If filtered samples had been taken, the entire trip would have yielded exactly 1.5 liters of sea water, a quantity which was insufficient. Therefore, the decision was made to abandon the filtering and to get as many other samples as possible. In a period of 1/2 hour, just under 40 liters of sea water was collected. The following procedures were used.

Prior to the actual sampling, the ship *Surveyor* was directed toward and allowed to drift into a current of water. A platform was lowered off the forward bow from which the samplings were made. Under these circumstances, the sampler was always between the ship's hull and the current of water.

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Under the prevailing conditions, contamination from the ship's hull would have been swept away from the sampler. While these were not ideal conditions they were the best possible under the circumstances.

After assembly, the sampler was rinsed off with distilled water from the Teflon bottles. The sampler was immersed in the sea water to a depth of about two meters, opened to collect the sample, closed, and then hauled up to the platform. The contents of the sampler were then transferred to a Teflon bottle. Several samplings were required to fill each bottle. Polyethylene gloves and bags were used to handle the equipment during these transfer steps. Additional bags were used to enshroud the bottle and sampler to help prevent particulate contamination from the atmosphere.

As soon as each bottle (unfiltered, either acidified or unacidified) was filled, it was placed in a cooler chest and surrounded by blocks of dry ice. Twenty liters of unfiltered, unacidified water were collected and frozen and approximately 16 liters of unfiltered and acidified (to 0.5N with ultra-pure  $\text{HNO}_3$ ) were collected and frozen. Some bottles containing  $\text{HNO}_3$  had leaked so these bottles were not used due to the loss of acid and the likelihood of contamination.

All bottles were stored in protective polyethylene bags with twist-tie closures at all times. The bottles were packed together with large amounts of dry ice in insulated boxes. On the return trip to Washington, DC, commercial deep freeze lockers were used during layovers to extend the lifetime of the dry ice. Upon arrival at NBS in Gaithersburg, Md., all samples were solidly frozen with large amounts of dry ice remaining. The samples were transferred to a large freezer maintained at  $-40\text{ }^\circ\text{C}$  and kept there until needed for analysis. Sample duplicates were provided to Dr. Burrell, University of Alaska, directly from this freezer.

Sample splits were received from the University of Alaska in a variety of ways. Most had been frozen at one time but were received at NBS (both water and sediment) in a thawed condition. Thawed samples were not re-frozen. Samples which were received frozen were stored at -40 °C. Certain samples were never frozen and were received and kept at room temperature. Most bottles had some degree of dirt on the outside since they were not sealed in polyethylene bags. This required that the outside of the bottle be cleaned prior to opening and sampling the contents. Sample splits received from the University of Alaska were both acidified and unacidified, filtered and unfiltered and were sampled from a variety of sites,

#### Preconcentration

The frozen sea water samples were thawed at room temperatures for approximately 12 hours. After the samples were completely thawed but were still below room temperature, they were inverted 40-50 times to assure homogeneity. Several samples exhibited inhomogeneity due to a residue of undissolved white crystals. The nature of these crystalline residues has been investigated and is included in this report. A 100 ml pycnometer was used to determine the density of a sea water sample which was found to be 1.018 g/ml.

Triplicate samples were obtained by weighing out  $101.8 \pm 0.2$  g ( $100.0 \pm 0.2$  ml) from the sample bottle into clean tared Teflon beakers. These beakers had been previously cleaned in hot (1+1) HCl for one day, hot (1+1) HNO<sub>3</sub> for one day and then were thoroughly rinsed in ultra-pure distilled water [28]. Known amounts of analytes were spiked to one sample from each triplicate set of sea water samples for the purpose of determining the recovery and to permit a check of the results.

The pH of the samples was determined using a Beckman Model SS-2 expanded scale pH meter equipped with Beckman glass and reference electrodes. A drop of pH 5 buffer was added to each sample and the sample pH was adjusted to pH 5.1-5.5 [29] using ultra-pure HNO<sub>3</sub> or NH<sub>4</sub>OH manufactured from NH<sub>3</sub> cylinder gas and ultra-pure water. The electrodes were washed with large volumes of ultra-pure water.

A column of 200-400 mesh Chelex 100 fitted with a 25 ml reservoir was cleaned using ultra-pure 2.5N HNO<sub>3</sub> [28]. The pH adjusted sample was loaded on the column by adding small portions of sample directly from the sample beaker to the column. The effluent flow rate under these conditions was 50 ml per hour. The column was washed with pH 5 buffer and ultra-pure water after all of the sea water sample had been passed through the column. After washing, the column was stripped of sample ions using ultra-pure 2.5N HNO<sub>3</sub> and the sample was collected in clean, tared 7 ml polyethylene bottles. The bottles were capped and re-weighed to determine the volume of their contents. Analytical blanks were carried through the same procedure [29].

**AAS Apparatus.** The instrumental system used in this study consists of a Perkin-Elmer Model 603 atomic absorption spectrometer with an HGA-2100 graphite furnace. The samples were introduced into the furnace with an AS-1 auto sampler. The instrumental parameters are given in Table 3.

**Reagents.** All standard stock solutions were prepared from high purity metals or salts in ultra high purity acids [28]. Working solutions were prepared as needed.

#### AAS Sample Preparation

Standard working solutions are prepared in ultra pure 1.25M HNO<sub>3</sub> from the standard stock solution. Aliquots of

B these solutions are then transferred to clean and dry sample cups on the AS-1 auto sampler. Duplicate aliquots of the unknowns are transferred to sample cups. To one cup an equal volume of ultra-pure water is added while to the second cup an equal volume of the analyte is added. The cups are then placed on the AS-1 turn-table and the AAS measurements are made automatically.

#### Measurement

The AAS instrument is turned on and the hollow cathode lamp for the analyte is inserted in the instrument and adjusted to the proper lamp current. The wavelength and slit widths are adjusted as listed in Table 3. The D<sub>2</sub> arc lamp is turned on and the two lamps are allowed to warm up for 15 minutes. Then the two beams are balanced. The AAS instrument is set on peak height and an integration time of five seconds. The other instrumental parameters are set as given in Table 3,

A calibration curve is established using three to five standard solutions with the AS-1 auto sampler. The calibration curve is repeated until the absorbance are within ±2 percent. Then the absorbance of the unknown solutions are measured using the bracketing technique. For example, the absorbance of a lower standard, the unknown, and then a higher standard is measured. This operation is repeated until the desired precision is attained. The net absorbance are obtained and a calibration curve is prepared using a least square fit on a hand calculator. The concentrations of the unknown are obtained from this calibration curve. If the recovery of the standard addition is not 100 percent, the concentration is corrected by the following equation:

$$c = x \cdot \frac{c}{y-x}$$

where  $x$  = rig/ml of analyte in the unknown as determined from the calibration curve.

$s$  = amount of standard added, rig/ml in final volume.

$y$  = rig/ml of analyte found in unknown with standard added as determined from the calibration curve.

$c$  = concentration, rig/ml.

## Results and Discussion

### Interferences

Interferences encountered with the graphite furnace can be classified as physical, chemical, and interelement in nature. Physical interferences are more pronounced with the graphite furnace than in most flame systems. Light scatter due to incomplete volatilization of inorganic compounds is of major importance. To minimize this type of interference, the time of charring is carefully controlled. However, if it persists, background measurements should be made with a continuum light source or at a nearby nonabsorbing line and then subtracted from the absorbance value obtained for the analyte.

Three possible mechanisms account for chemical interferences. The analyte may be lost by the formation of a volatile compound, by occlusion in a nonvolatile matrix, and by the formation of carbides. As an example, lead chloride which boils at 950 °C has a considerable vapor pressure at lower temperatures and can be lost in the charring step. Therefore, the nitrate ion is preferred for graphite furnace AAs. The standards must be prepared in the same concentration of anion as the analyte. As an example, when the absorbance of 1 ng of Pb in 0.5 and 10 percent HNO<sub>3</sub> were compared, the 10 percent HNO<sub>3</sub> suppressed the lead absorbance by 40 percent. Another major interference is from the reaction of the furnace

material to form nonvolatile metal carbides. Although carbide formation does occur, it can be controlled with the use of a pyrolytic coating on the inner surface of the graphite rod.

The interelement effect is more pronounced in the flameless technique than in flame systems. It occurs when the analyte reacts with another element which may produce a suppression at certain atomic ratios and an enhancement under certain other conditions. This type of interference can sometimes be corrected by the standard addition method; however, the best technique is to prepare the standards in a similar matrix as the unknowns.

#### Matrix Modification

In sea water the high salt content makes it difficult to volatilize effectively the matrix without loss of the analyte. The major component, sodium chloride, has both a relatively high volatilization temperature (B.P. 14-15 °C) and heat of formation (AH, 98 kcal/mole). In order to char such a matrix, the components have to be volatilized and then either decomposed or diffused out of the graphite cell in a manner which precludes loss of the analyte. Also, trace metals in sea water are present mainly as the chlorides which have a lower volatilization temperature than sodium chloride.

To overcome this difficulty Ediger et al. [30] proposed the technique of matrix modification for the determination of a series of elements in sea water. They added an aliquot of a 50 percent solution of ammonium nitrate to the sample in the graphite furnace which assists in the removal of the sodium chloride during the charring cycle. The ammonium nitrate converts the sodium chloride to a more volatile compound. However, in most preconcentration steps the calcium and magnesium are also concentrated and the ammonium nitrate had little or no effect on these elements.

In this study the matrix modification technique was not completely satisfactory. First of all, the trace elements of interest in the Gulf of Alaska are below the detection limit of the graphite furnace AAS and a preconcentration step is required. Also, the 'trace impurities found in ACS reagent grade ammonium nitrate far exceeded the trace concentrations in the sea water. While ammonium nitrate can be purified using Chelex 100 resin, this type of matrix modification does not alleviate the interference of calcium and magnesium.

In our initial studies the separation technique of Riley and Taylor [21] using Chelex 100 resin was evaluated. The recovery of trace elements of interest based on radioactive nuclei was greater than 99 percent. When this technique was applied to the samples of sea water, calcium and magnesium were also preconcentrated which produced a severe suppression of the analyte by AAS. To alleviate this difficulty a separation procedure was developed, as described above in the section on preconcentration, which removed the alkaline earth metals.

#### Applications

The preconcentration and graphite furnace AAS method described has been applied for the determination of Cd, Mn, Ni, and Pb in sea water. The results are given in Table 4. Each value represents the concentration of the analyte carried through the procedure and not duplicate determinations of a single test portion. As a check of the recovery of the separation a known concentration of the analyte was added to a third test portion and processed along with the two unknowns. The recovery of the spiked analytes was 80 to 120 percent. It was concluded that variability of analytical blank was the major contributing factor for the deviation in results.

The cadmium values for all the NBS collected samples were less than 0.01 rig/ml which represents our detection limit by graphite furnace AAS when the trace metals are pre-concentrated by a factor of 20. Since the reagent blanks for cadmium was not a limiting factor, a positive value could be obtained if a larger sample was pretreated and concentrated,

For lead the reagent blank was 0.1 ng which determined the detection limit. If larger samples were preconcentrated without the use of additional reagents, the detection limits for lead could be lowered. The major difficulty for lead is contamination as exemplified in sample EGA 11. It is very likely the 0.08 rig/ml of lead is due to contamination.

The effect of acidification before and after filtration is clearly shown when comparing manganese values in NBS 500 and 502 with NBS 509 and 518. These results show that acidification caused the Mn concentration to increase by at least a factor of two. The reagent blank for manganese is less than 0,02 ng which would certainly not be a contributing factor. In one sample, NBS 509, the lead value was several orders of magnitude higher than the unacidified samples. The addition of 44 g of HNO<sub>3</sub> to a liter of sea water as in NBS samples 509 and 518 was calculated to be insignificant for Cd, Mn, Ni and Pb [28].

The nickel reagent blank (0.2 ng) was the highest of the analytes tested. Since the nickel values in sea water were considerably higher, this high reagent blank was not considered a serious problem.

Sample Inhomogeneity Caused by Crystallization. Inhomogeneity was found in four samples; two samples from the University of Alaska and two of the NBS samples. These two NBS samples were not analyzed; other, homogeneous samples were substituted from the same site. The samples upon thawing had noticable white and clear crystals at the bottom

of the sample bottle. In each case the samples were unfiltered and not strongly acidic (see Table 5). EGA 24 was the only sample in which the crystals redissolved at room temperature. In the remaining samples with crystalline precipitates the precipitate was stable at room temperature and did not dissolve.

The crystals were extracted from NBS Bottle Number 3 and dried in a Teflon beaker. Upon addition of nitric acid, a violent evolution of gas was noted accompanied by instantaneous volubility. The solution was evaporated to a single drop in Teflon and subjected to spark source mass spectrometry. The dominant cation was found to be Ca. Small amounts of Na, K, and Mg were found, probably resulting from absorption to the surfaces of the crystals. No amounts of heavy metal or trace ions were found. This coupled with the evolution of gas upon acid addition would indicate that the dominant species would be a hydrated calcium carbonate ( $\text{CaCO}_3 \cdot x\text{H}_2\text{O}$ ).

The crystals were too numerous and of sufficient mass not to be noticed in the original sampling. It is much more likely then that they were formed in the sample during storage and handling. No crystals were noticed in strongly acid samples which would be expected since the low pH would preclude their formation.

Why the crystals were found in some samples and not others of similar character is unclear. No other perceptible difference between the homogeneous and inhomogeneous samples was obvious except for the crystals. There were samples from the University of Alaska and NBS of equal or higher pH which did not contain crystals. The fact that only unfiltered samples were subject to this phenomenon could indicate nucleation or some other aspect of solid particle influence aiding the formation of the crystals.

Samples EGA 24 and EGA 15 were analyzed and there is no evidence to indicate that the inhomogeneity caused by the crystals caused any significant alteration in the results in relation to samples of the same general area. Any effect would, however, have to be one to two orders of magnitude larger before obvious alterations could be detected with these unknown samples.

#### Summary

As a result of work reported here and elsewhere it has been determined that a number of plastic materials may be suitable for the collection and storage of samples of sea water [27]. It has been demonstrated, for example, that conventional polyethylene containers if properly cleaned do not materially contribute to inorganic trace metal contamination and if protected from vapor losses are probably suitable for at least several years storage. Problems of contamination which might appear upon long term storage have not been resolved. It would appear that immediate freezing of water samples and storage of these in the frozen state until analysis is to be recommended.

It is shown here that analysis for a variety of elements may be done accurately on as little as 100 ml of water even in the extremely clean waters of Alaska using graphite furnace atomic absorption spectrometry, if extreme care is taken to prevent contamination during the preconcentration procedure. A new preconcentration procedure has been developed here which should substantially help in these analyses in that only minimal handling of the sample is required, only reagents for which ultra purification procedures are available are required and the procedure appears adaptable to field or shipboard use. In addition, the procedure removes elements (i.e., Na, K, Ca,

and Mg) that are interferences in many analytical methods and thus makes possible the use of a variety of techniques such as atomic absorption (flame or blameless), neutron activation and x-ray fluorescence.

#### Suggestions for Future Work

Because of the very low level of trace elements in sea water the accurate analyses of these is a difficult job under even ideal conditions. The problems in preventing contamination during the analysis are severe. Those encountered during the collection and storage are even more formidable. It is believed that progress has been made in the area of storage and may be minimized by the proper cleaning of containers and by freezing the samples as soon as possible.

Preventing contamination during collection, however, requires much attention. If only total elemental concentrations are required, that is, no distinction between suspended and dissolved elements is to be made, then acidification simultaneously with collection, followed by freezing, may be used as shown here. If, however, filtration is to be done to distinguish between suspended and dissolved elements then it is apparent from this work that the filtration must be done as the sample is collected. Sampler-filters such as that of Harrison et al. [25] accomplish this for shallow water collection effectively but are not applicable (in the present state) for duplicate water collection and are difficult to use in a harsh environment. We believe that an effective technique may be to filter and preconcentrate the samples in one step as collection procedures using an adaptation of the Chelex 100 procedure reported here and are proceeding with this work.

In order to describe adequately materials and experimental procedures, it was occasionally necessary to identify commercial products by manufacturers' name or label. In no instance does such identification imply endorsement by the National Bureau of Standards nor does it imply that the particular products or equipment are necessarily the best available for that purpose.

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Table 1. Organic Ligands used to Separate Trace Elements in Sea Water.

| <u>Organic Li gand</u> | <u>Solvent</u>       | <u>Element</u>                                   |
|------------------------|----------------------|--|
| APDC [11-16]           | MIBK "               | Bi, Cd, Co, Cr,<br>Cu, Fe, Hg, Mn,<br>Ni, Pb, Zn |
| NaTφB [8]              | MIBK-<br>Cyclohexane | Cs, Rb   |
| Oxine [11]             | MIBK                 | Mg, Mn, Ni                                       |

APDC - Ammonium pyrrolidene dithiocarbamate

NaTφB - Sodium tetraphenylboron

Oxine - 8-hydroxyquinoline

Table 2. Volubility of Solvents in Water [17].

| <u>Solvent</u>           | <u>Volubility, ml/l at 25 °C</u> |
|--------------------------|----------------------------------|
| Ethyl Acetate            | 9                                |
| MIBK                     | 20                               |
| Cyclohexane              | <<1                              |
| 2-Butyl Alcohol          | 155                              |
| Methyl Isobutyl Carbinol | 22                               |

Table 3. Instrumental Parameters.

| Element | Wavelength<br>nm | - P&E 603 - - - - - |                    | -HGA-2100 - - - - -  |                        |                           |
|---------|------------------|---------------------|--------------------|----------------------|------------------------|---------------------------|
|         |                  | SBW<br>nm           | Scale<br>Expansion | Drying<br>Temp./Time | Charring<br>Temp./Time | Atomization<br>Temp./Time |
| Cd      | 228.8            | 0.7                 | 1                  | 100/30               | 200/20                 | 2100/7 <sup>a</sup>       |
| Mn      | 279.5            | 0.7                 | 2.0                | 100/30               | 300/30                 | 2700/7 <sup>a</sup>       |
| Ni      | 232.0            | 0.7                 | 7.0                | 100/40               | 1000/30                | 2700/6 <sup>a</sup>       |
| Pb      | 283.3            | 0.7                 | 3.0                | 100/40               | 400/30                 | 2200/7 <sup>b</sup>       |

<sup>a</sup> Inert gas in the Interrupt mode.

<sup>b</sup> Inert gas in the Normal mode.

Note: Temperatures are in °C; Time in seconds.

Table 4. Analysis of Cadmium, Lead, Manganese, and Nickel in Sea Water.

| Sample/Location    | Sample Treatment <sup>a</sup> | Original pH | - - - - -rig/ml - - - - - |       |      |       |
|--------------------|-------------------------------|-------------|---------------------------|-------|------|-------|
|                    |                               |             | Cd                        | Mn    | Ni   | Pb    |
| WGA, Station 1:2   | F,A,b                         | 1.7         | 0.14                      | 0.72  | 0.65 | 17    |
|                    |                               |             | 0.05                      | 0.68  | 0.78 | 11    |
| EGA 24<br>(410 m)  | F,A                           | 3.5         | 0.11                      | 0.05  | 0.24 | 0.02  |
|                    |                               |             | 0.10                      | 0.06  | 0.32 | 0.05  |
| WGA 110<br>(173 m) | F,A                           | 5.1         | 0.07                      | 0.22  | 0.36 | 0.20  |
|                    |                               |             | 0.13                      | 0.28  | 0.34 | 0.32  |
| EGA 11<br>(135 m)  | F,A                           | 5.2         | 0.05                      | 0.03  | 0.27 | 0.08  |
|                    |                               |             | 0.06                      | 0.03  | 0.29 | <0.02 |
| WGA 110<br>(173 m) | UF,A                          | 5.4         | 0.09                      | 0.18  | 0.41 | <0.02 |
|                    |                               |             | 0.08                      | 0.18  | 0.45 | <0.02 |
| EGA 15<br>(1500 m) | F,A                           | 6.6         | 0.10                      | <0.02 | 1.7  | <0.02 |
|                    |                               |             | 0.14                      | <0.02 | 0.8  | <0.02 |
| EGA 24<br>(410 m)  | UF,A                          | 3.6         | 0.12                      | 0.02  | 0.49 | <0.02 |
|                    |                               |             | 0.13                      | 0.02  | 0.40 | <0.02 |
| EGA 11<br>(1350 m) | UF,A                          | 6.8         | 0.11                      | <0.02 | 0.36 | <0.02 |
|                    |                               |             | 0.12                      | <0.02 | 0.38 | <0.02 |
| EGA 15<br>(1500 m) | UF,A                          | 5.4         | 0.13                      | <0.02 | 0.90 | <0.02 |
|                    |                               |             | 0.12                      | <0.02 | 0.78 | <0.02 |
| NBS 500            | Fc,UA                         | 7.3         | <0.01                     | 0.45  | 1.2  | 0.18  |
|                    |                               |             | <0.01                     | 0.37  | 1.7  | 0.17  |
| NBS 500            | UF,UA                         | 7.2         | <0.01                     | 0.59  | 0.90 | <0.02 |
|                    |                               |             | <0.01                     | 0.67  | 0.70 | <0.02 |
| NBS 502            | Fc,UA                         | 8.3         | <0.01                     | 0.40  | 0.49 | <0.02 |
|                    |                               |             | <0.01                     | 0.46  | 0.53 | <0.02 |
| NBS 502            | UF,UA                         | 8.2         | <0.01                     | 0.71  | 0.66 | <0.02 |
|                    |                               |             | <0.01                     | 0.64  | 0.71 | <0.02 |
| NBS 509            | UF,A                          | (3.4        | <0.01                     | 1.3   | 0.45 | 4.5   |
|                    |                               |             | <0.01                     | 1.4   | 0.59 | 5.8   |
| NBS 518            | UF,A                          | 1.3         | <0.01                     | 1.4   | 0.41 | <0.02 |
|                    |                               |             | <0.01                     | 1.3   | 0.45 | <0.02 |

<sup>a</sup> All samples stored frozen except b which was stored at ambient temperature. F-filtered, Fe-filtered after thawing, A-acidified, UF-unfiltered, UA-unacidified. Less than values are AAS detection limits based on 100 ml test portion.

Table 5. Samples Having Crystalline Precipitates.

| <u>Sample</u>               | <u>Sample Preparation</u>          | <u>pH of Samples after Thawing</u> |
|-----------------------------|------------------------------------|------------------------------------|
| <u>University of Alaska</u> |                                    |                                    |
| EGA 24                      | unfiltered, acidified,<br>frozen   | 3.6                                |
| EGA 15                      | unfiltered, acidified,<br>frozen   | 6.7                                |
| <u>NBS Samples</u>          |                                    |                                    |
| Bottle No, 3                | unfiltered, unacidified,<br>frozen | 8,2                                |
| Bottle No. 507              | unfiltered, unacidified,<br>frozen | 8.2                                |

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## SAMPLING AND SAMPLE HANDLING FOR ACTIVATION ANALYSIS OF RIVER WATER

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A complete preanalysis scheme for determining trace elements in river and estuarine water by instrumental neutron activation analysis is described. The design, operation and evaluation of a new Teflon water sampler is included in the presentation of the preanalysis scheme. The evaluation of this water sampler consists of replicate sampling experiments and a comparison with a commercial sampling bottle (VanDorn). The water sampler described allows for filtration of the sample as it is transferred from the sampler to a storage container. Lyophilization (freeze drying) is used as the preconcentration technique for the dissolved species, *i.e.* liquid portion of the sample. Normalization of suspended particulate data to the element scandium is presented as a useful technique for locating man-made heavy metal input sources,

Keywords: Filtering water; river water; sampling water for trace elements; suspended particulates in water; Teflon water sampler; trace elements; trace elements in water; water.

### I. Introduction

The current interest in sampling and sample handling for trace constituents is evidenced by the large attendance at this symposium. Previous speakers have discussed general problems associated with trace element sampling and sample handling so this point will not be belabored.

Sampling for trace elements is difficult in any matrix. However, if some component of the geochemical environment is to be investigated, the sam-

pling problems are exceedingly more difficult than for most synthetic materials, which may be homogeneous. In the environment, the system sampled is generally *not* homogeneous over the area of interest. The fluid systems, water and air, are in a state of continuous chemical and physical change, even during their sampling and storage. Therefore, obtaining and storing representative samples are not considered trivial problems.

In this work, an attempt was made to develop and evaluate a preanalysis scheme for trace elements in water. This includes [he sampling protocol, as well as storage and handling techniques. If such a research technique can be evaluated thoroughly and quantitatively, it should be useful in studying less expensive and faster protocols which may be necessary for environmental surveillance work.

The preanalysis design presently used in this laboratory consists of an all Teflon, Teflon-coated metal, and nylon sampler to minimize contamination from construction materials. After sampling, immediate filtration is carried out in the field followed by fast freezing of the aqueous portion of the sample in liquid nitrogen. Upon return to the laboratory, samples are stored frozen and, prior to analysis by neutron activation, are preconcentrated by freeze drying.

When designing this scheme of sampling and sample handling it was felt that the total number of liquid sample transfers must be kept to a minimum to avoid unnecessary random sources of contamination. This goal was achieved by keeping the total number of sample transfers to one.

## II. Procedure

The NBS water sampler is illustrated in figure 1. The sampler consists of a horizontal Teflon cylinder mounted on an "ice clamp action" type of frame, with flat Teflon end caps in place of what would be ice hooks. The frame, though made of metal (aluminum and stainless steel), has a baked-on Teflon coating. The Teflon cylinder has an interior thread on one end (fig. 2) to provide for attachment of a filtering mechanism, to be described below. A Teflon-coated rudder may be attached to the bottom of the cylinder to allow its proper orientation with the current flow'. All parts of the sampler are assembled with nylon screws, bushings, washers, *etc.*

One of the unique features of the sampler is that it provides an option for sample filtration during the transfer to the storage container. A Teflon adaptor is threaded to mate the sampling cylinder with a polycarbonate filter holder. The components of this filtering mechanism are pictured in figure 3.

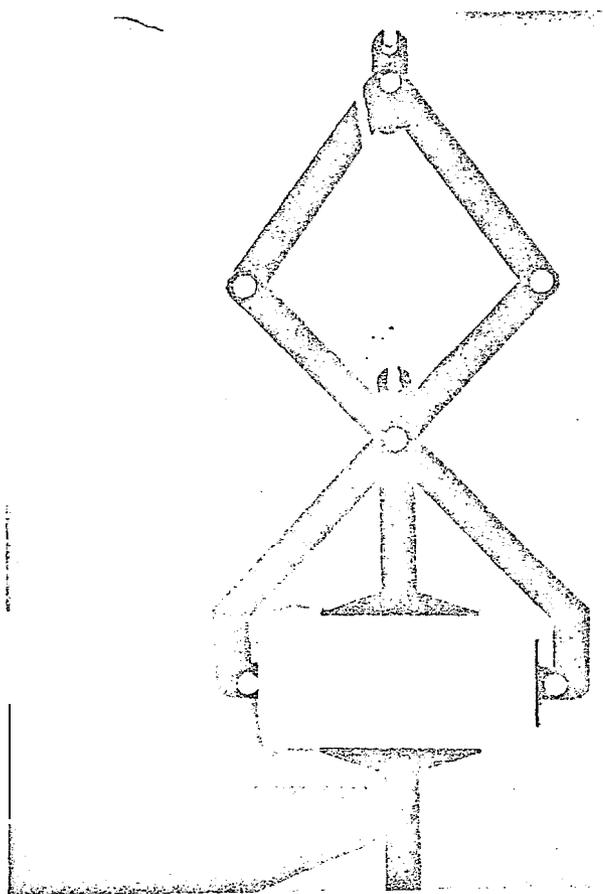


Figure I. Teflon water sampler in vertical, closed position.

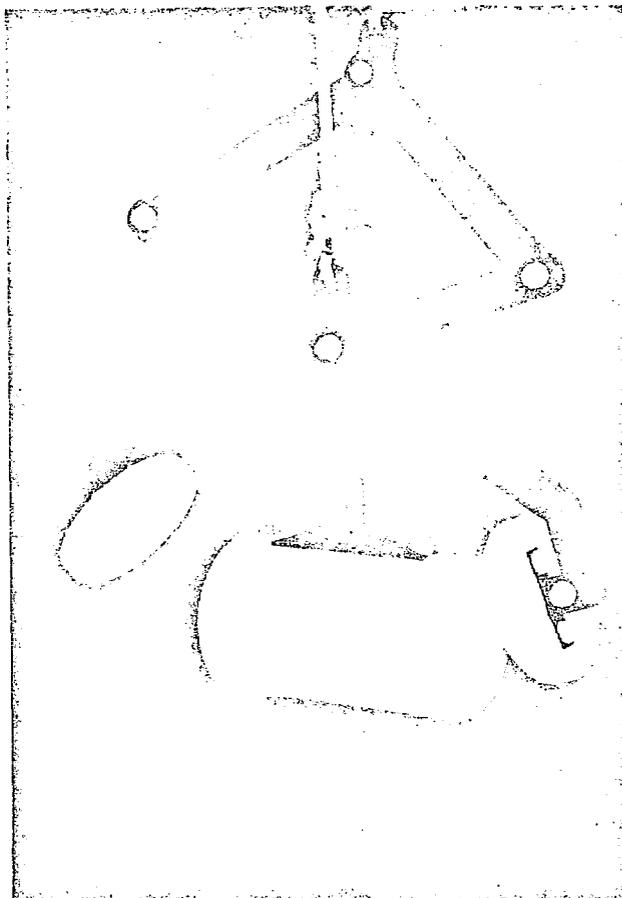


Figure 2. Teflon water sampler in vertical, partially open position, showing interior threads for attachment of filtering unit.

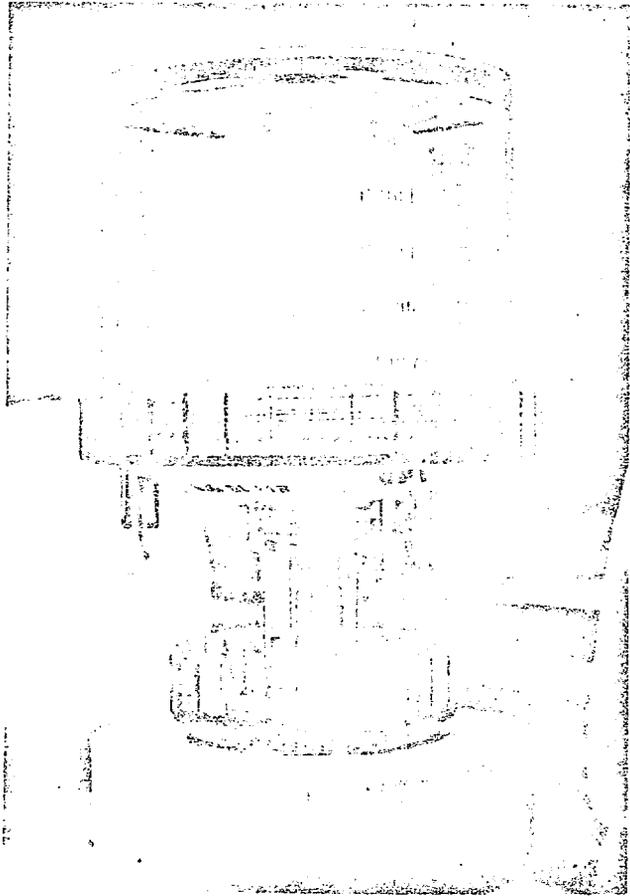


Figure 3. Attachment of polycarbonate filtering unit to filled water sampler through use of Teflon adaptor.

Generally, the filters used are a 47 mm diameter, 0.4  $\mu\text{m}$  pore Nuclepore filter covered with a 47 mm diameter, 8  $\mu\text{m}$  pore Nuclepore filter as a roughing filter. The filters are sealed between the Teflon adaptor and the filter support with a silicone O-ring. The receiver flask attached below the filter holds a polyethylene film bag. This bag serves as the sample container throughout the storage, freeze drying and analysis procedure. A hand pump is used to provide the vacuum for filtration in the field, e.g., from a 14-ft rowboat. The complete sampling system assembled and ready for filtration is shown in figure 4.

One of the main advantages of the NBS water sampler is its capability of being lowered below the water surface in a closed configuration, avoiding contamination of the inner surface of the sampler with possible surface slicks or microlayers. After lowering the sampler to a depth of about 0.3 meters it may be opened by pulling a second rope. The sampler is then lowered to the desired depth and allowed to equilibrate. The first rope is pulled to close the end caps and the water sample is brought back to the surface.

After attaching the filtering unit the sample may be filtered directly from the Teflon cylinder into the polyethylene storage bag. This is the only sample transfer in the entire procedure. The liquid sample contained in the polyethylene bag is frozen in the field in liquid nitrogen and stored in a cleaned plastic bag. The filters containing the suspended particulates are transferred to a cleaned plastic petridish. Both the frozen liquid and filter portions of the sample are stored in dry ice until returning to the laboratory where they are transferred to a freezer.

The frozen liquid samples are prepared for analysis by preconcentrating using lyophilization (freeze drying). The technique for freeze drying has been described in detail elsewhere [1,2], however, a brief description may be appropriate here. The basic freeze drying unit, shown in figure 5, consists of a sample chamber, cold trap and source of vacuum. The frozen sample, still in the polyethylene film bag, is placed in the chamber which is then opened to the vacuum line. During the freeze drying process, water sublimates and a residue of solids accumulates at the bottom of the bag. After the process is finished the bag is folded up with the residue sealed inside, to make a small package for neutron irradiation.

Considerable work has been completed to evaluate the retention yields of trace elements during freeze drying. The results appear satisfactory for all elements investigated except for mercury and iodine (fig. 6). Recently, Filby, Shah and Funk [3] reported quantitative retention of mercury in a tracer study of the lyophilization of water.

<sup>1</sup>The NBS water sampler must be operated by two ropes, one supports the weight of the sampler while holding the end caps against the cylinder, the other supports its weight using it to pull the end caps up and away from the cylinder allowing for an uninterfered flow-through system.

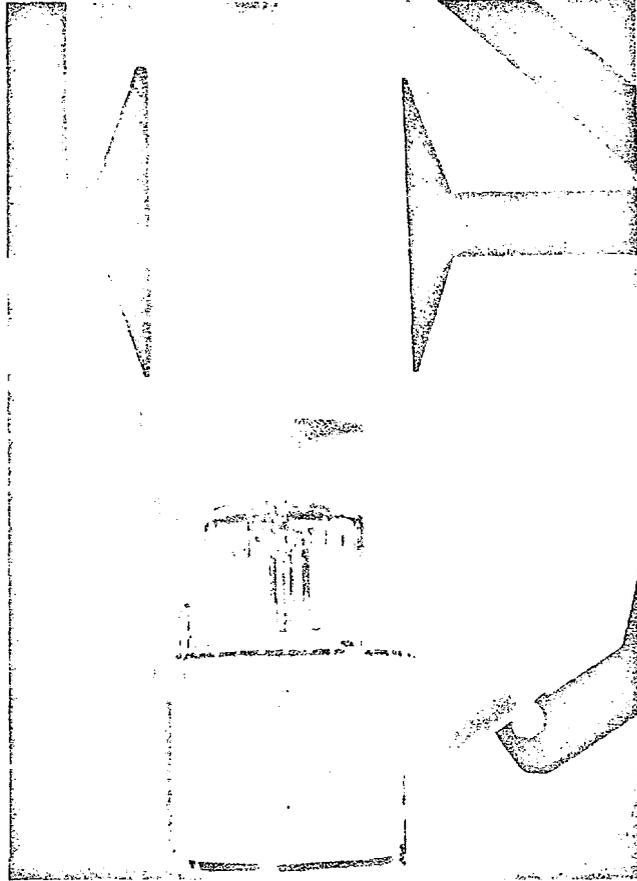


Figure 4. Teflon water sampler with filtering apparatus attached, ready for vacuum filtration into a clean polyethylene storage bag inside the filtering unit.



### III. Results and Discussions

One of the main objectives of this work was to determine variability of data due to sampling. The approach used was to take replicate samples from a given location over as short a period of time as possible, usually 2 to 4 hours. It should be pointed out that in a field experiment it is difficult to distinguish between concentration variations due to time or position. In an estuarine or river system it is almost impossible to sample the same water mass over a 2- to 4-hour time interval.

The first station chosen for this kind of work was the Patuxent River at Laurel, Maryland. At this point the river is just a fresh water stream and it was necessary to wade to midcurrent to obtain the samples. Of course, bottom sediment is stirred up when wading but due to a rather swift current that day the disturbance created by wading subsided in several minutes and a sample could be taken upstream to minimize these effects.

At this location eight samples were taken. That is, eight separate wadings to midstream were made with processing of each sample on shore before the next one was initiated. Obviously, these replicate samples could not be considered to be taken from exactly the same body of water.

The results of instrumental neutron activation analysis (INAA) of the Laurel samples appear in tables 1 and 2. For the dissolved species, the coefficients of variation for the 13 elements determined in these "replicate samples" vary from a surprisingly low 3.0 percent for manganese to 80 percent for cobalt. A few outliers are obvious, cobalt in sample L-13 and chlorine in sample L-9. The high cobalt value in L-13 does not correlate with high values for scandium, iron, or thorium, elements which would be present in crustal particulate contamination. The low value for chlorine in sample L-9 is equally unexplainable. A low value of a halide in water might be explained by oxidation to the elemental form and volatilization during freeze drying. This idea is untenable since the bromide ion is more readily oxidized than chloride ion, and the value obtained for bromine in L-9 is just below one standard deviation from the average. Of these eight samples, originally weighing from 60 to 90 grams each, nine of the 13 elements determined exhibited coefficients of variation of 20 percent or less.

The results of INAA of the Laurel suspended particulates are shown in table 2. These samples were collected, freeze dried, irradiated and counted on polycarbonate film filters. Only the first six of the suspended particulate samples were analyzed for some of the elements which have long radioactive half-lives on irradiation. Technical difficulties prevented the analysis of the others. The elements measured in the suspended particulates have been normalized to scandium which is an element which



TABLE 2. Concentration of suspended particulates in Laurel samples

| Number                   | Elements                  |                           |                          |                           |                           |                           |                           |                           |                           |                           |
|--------------------------|---------------------------|---------------------------|--------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
|                          | Al<br>( $\mu\text{g/g}$ ) | Mn<br>( $\mu\text{g/g}$ ) | v<br>( $\mu\text{g/g}$ ) | c1<br>( $\mu\text{g/g}$ ) | Na<br>( $\mu\text{g/g}$ ) | Sc<br>( $\mu\text{g/g}$ ) | Fe<br>( $\mu\text{g/g}$ ) | co<br>( $\mu\text{g/g}$ ) | Th<br>( $\mu\text{g/g}$ ) | Sb<br>( $\mu\text{g/g}$ ) |
| L-8 P                    | 2.34                      | 23.8                      | 3.79                     | 15.9                      | 4.57                      | 0.366                     | 1.36                      | 0.542                     | 0.367                     | 0.014                     |
| L-9P                     | 2.20                      | 20.9                      | 2.80                     | 18.3                      | 6.17                      | .345                      | 1.25                      | .552                      | .306                      |                           |
| L-10P                    | 2.50                      | 27.0                      | 3.67                     | 21.3                      | 6.69                      | .405                      | 1.38                      | .605                      | .354                      | .032                      |
| L-11P                    | 2.55                      | 23.9                      | 2.76                     | 14.7                      | 10.8                      | .370                      | 1.36                      | .534                      | .357                      | .016                      |
| L-12P                    | 2.24                      | 21.3                      | 3.20                     | 11.3                      | 5.38                      | .359                      | 1.27                      | .510                      | .409                      | .0093                     |
| L-13P                    |                           | 25.3                      |                          | 13.9                      | 6.57                      | .360                      | 1.25                      | .507                      | .392                      | .012                      |
| L-14P                    | 2.30                      | 24.6                      | 3.53                     | 14.7                      | 7.95                      |                           |                           |                           |                           |                           |
| L-15P                    | 2.66                      | 25.0                      | 3.64                     | 30.2                      | 8.61                      |                           |                           |                           |                           |                           |
| Average                  | 2.40                      | 24.0                      | 3.34                     | 17.5                      | 7.09                      | .368                      | 1.31                      | .542                      | .364                      | .017                      |
| CV <sup>a</sup> , %      | 7.2                       | 8.5                       | 13                       | 34                        | 28                        | 5.5                       | 4.7                       | 6.6                       | 9.8                       | 52                        |
| CV/[Sc] <sup>b</sup> , % | 4.4                       | 6.2                       | 13                       | 19                        | 32                        |                           | 3.4                       | 4.8                       | 11                        | 47                        |

<sup>a</sup> Coefficient of variation.

<sup>b</sup> Coefficient of variation when the average elemental concentration is ratioed to the scandium concentration.

may be indicative of contributions due to clay particles and crusts] weathering from natural sources. This is a procedure which has been used in transport studies of heavy metals in sediment [4]. The coefficient of variation is improved for nearly all elements when values are normalized to scandium, with only slight increases for the exceptions, thorium and sodium.

The fast moving fresh water stream at Laurel appears to be a well-mixed system and a single 50 to 100 gram sample under these conditions generally gives a relative standard deviation of 20 percent or less at concentrations down to the subnanogram/gram level for the elements analyzed.

A set of samples similar to those taken at Laurel were taken from the side of a boat anchored at the mouth of the Susquehanna River in the Chesapeake Bay (Turkey Point). In figure 7 are illustrated the results of the suspended particulate taken from this estuarine location. Again, for suspended particulates, the coefficient of variation for each element is significantly diminished (with the exception of manganese) when the data is normalized to scandium.

The importance of normalizing data obtained from suspended particulate using an element indicative of purely crustal weathering or natural sources is illustrated in figures 8, 9, and 10. In figure 8 is presented results for chromium in the suspended particulate of the Back River, just east of Baltimore, Maryland. A very large sewage treatment plant is located on the Back River, Station 1 is at the mouth of the river, which flows into the Chesapeake Bay. Station 6 is directly in the plume of the midstream effluent outfall of the sewage treatment plant. When the chromium concentration is plotted with respect to distance (as approximated by station number) from the effluent outfall a slight rise is observed as station 6 is approached. (Plotting the chromium data with respect to salinity instead of distance from effluent outfall gives an almost identical curve.) However, if the data is normalized to scandium a much more striking increase is seen as one approaches the plant effluent outfall. This indicated that there is an anthropogenic source of chromium in the particulate material coming from the sewage treatment plant or another upstream location.

Iron in the Back River exhibits a similar behavior and is shown in figure 9. However, in the case of iron no concentration gradient is observed in proceeding upstream from the mouth of the river. On the other hand, normalization against scandium shows a pronounced upstream gradient which apparently indicates a source of noncrustal iron upstream.

When the concentration of thorium and of thorium relative to scandium are plotted for the Back River suspended particulate (fig. 10), only a smoothing out of the data is obtained by normalizing to scandium, indicat-

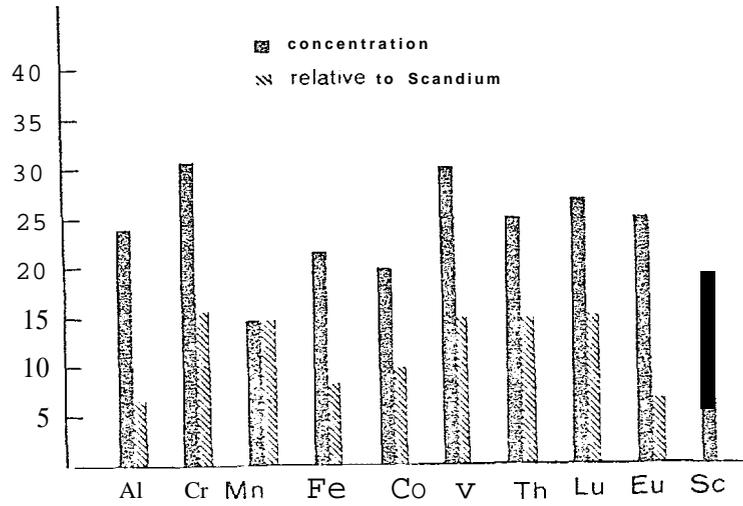


Figure 7. Coefficients of variation for trace elements from replicate samples of estuarine water, suspended particulate only.

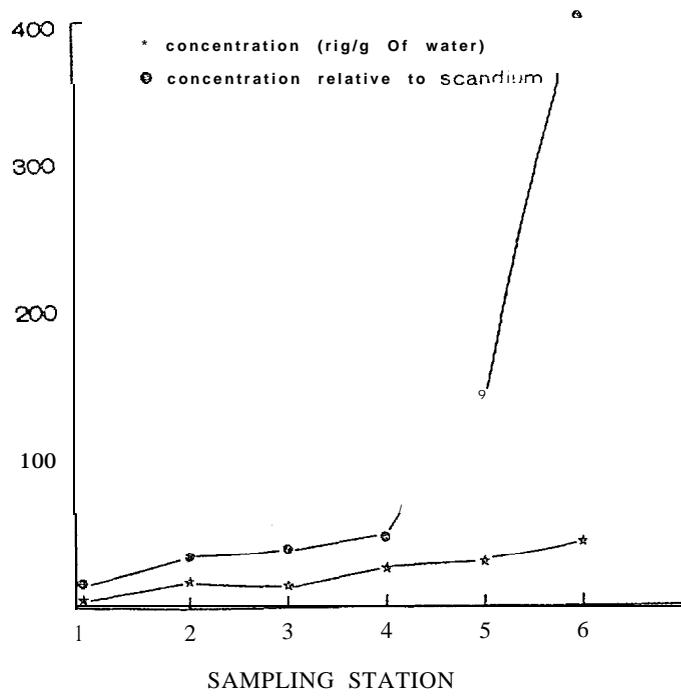


Figure 8. Chromium in back river suspended particulates.

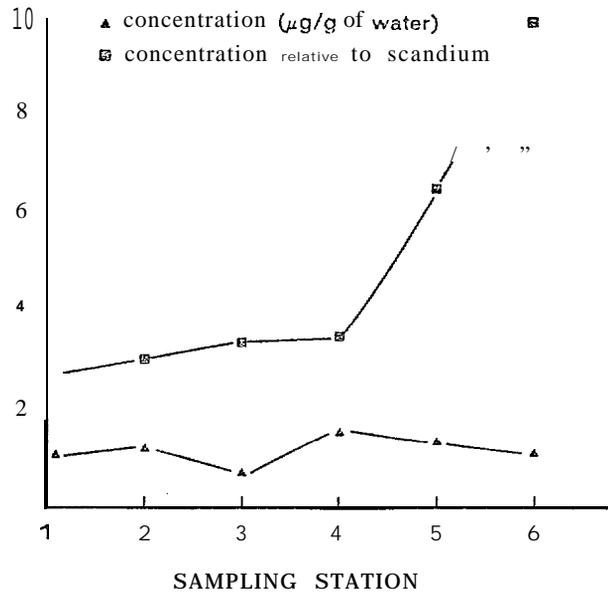


Figure 9. Iron in Hack River suspended particulate.

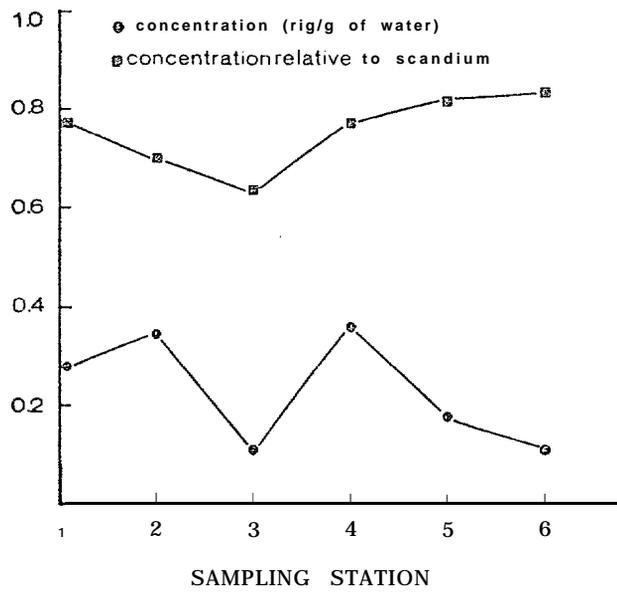


Figure 10. Thorium in Hack River suspended particulates.

ing no significant input of thorium from an anthropogenic source. It is felt that the added information obtained by this normalization technique should be useful in detecting sources of man-made heavy metal input.

In the Susquehanna River experiment, replicate samples taken with the NBS sampler were compared to samples taken with a Van Dorn commercial sampler. This particular Van Dorn sampler was part of the routine equipment on the research vessel used for this experiment and it is likely that the sampler has been used at least 3 days a week and up to 10 times a day for the past several years. The sampler was therefore expected to contaminate the samples. The results are found in table 3 in the chronological order in which they were taken. It has already been mentioned that it is very difficult to get a body of water to stay still during a replicate sampling experiment. This difficulty is demonstrated by noting the values for sodium in table 3. The sampling had begun at low tide, but the tide soon started coming in, leading to increasing salinity during the sampling period and possibly stirring up some of the bottom sediments.

The comparison of data for Van Dorn samples (VD 1, VD 2, VD 3) to those for our Teflon sampler (NBS 1, NBS 2, NBS 3, NBS 4, NBS 5) seems to indicate that the commercial sampler is contributing little if any contamination to the sample at the concentration levels found here. This may be explained in two ways: The sample from the Van Dorn was transferred immediately (< 3 min) to the Teflon cylinder for filtration, leaving very little time for container-sample interactions. Alternatively, this particular Van Dorn sampler, which is made of PVC, rubber and surgical tubing, could have been used so often that all or most of the leachable contaminants had since been removed and it had reached an equilibrium with Chesapeake Bay water.

Other interesting features of the data in table 3 are the inconsistently high values for cobalt, iron and scandium in samples VD 3 and NBS 4. This could be suspended particulate contamination due to improper filtration or external contamination. These high values could also be real and caused by the disturbance of the sediments with the changing tide. In addition, the variability in samples from fresh water streams seems less than for samples from estuarine water, over a short timespan.

It is felt that the evaluation of the sampling of natural water using this system has just begun. Further work in evaluating the sampling of river and estuarine water is planned as well as initiating sampling studies in coastal ocean water.

TABLE 3. Trace element concentrations in replicate samples of estuarine water  
(Dissolved Species Only)

| Sample             | Zn<br>( $\mu\text{g/g}$ ) | Sr<br>( $\mu\text{g/g}$ ) | Co<br>( $\mu\text{g/g}$ ) | Fe<br>( $\mu\text{g/g}$ ) | Se<br>( $\mu\text{g/g}$ ) | Ag<br>( $\mu\text{g/g}$ ) | Sc<br>( $\mu\text{g/g}$ ) | Na<br>( $\mu\text{g/g}$ ) |
|--------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| NBS <sup>a</sup> 1 | 2.6                       | 94                        | 0.22                      | 28                        | 0.18                      | 0.07                      | 0.011                     | 4.5                       |
| VD <sup>b</sup> 1  | 8.9                       | 108                       | .20                       | 36                        | .14                       | .86                       | .008                      | 6.6                       |
| NBS2               | 4.0                       | 117                       | .27                       | 44                        | .15                       | .39                       | .017                      | 34                        |
| VD2                | 6.3                       | 101                       | .24                       | 38                        | .13                       | .27                       | .009                      | 43                        |
| NBS3               | 3.9                       | 121                       | .27                       | 46                        | .21                       | .12                       | .024                      | 44                        |
| VD3                | 7.1                       | 121                       | .44                       | 122                       | .14                       | .42                       | .034                      | 45                        |
| NBS4               | 12                        | 115                       | .67                       | 266                       |                           | .15                       | .28                       | 48                        |
| NBS5               | 11                        | 92                        | .26                       | 44                        |                           | .90                       | .024                      | 36                        |

<sup>a</sup> NBS = National Bureau of Standards samples.  
<sup>b</sup> VD = Van Dorn samples.

#### IV. Acknowledgements

We are especially grateful to James Suddueth of the Analytical Chemistry Division at NBS for the design for this water sampler.

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# Production and Analysis of Special High-Purity Acids Purified by Sub-Boiling Distillation

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Sub-boiling distillation from pure quartz or Teflon (Du Pont) stills has been investigated for the production of high-purity inorganic acids and water. Nitric, hydrochloric, hydrofluoric, perchloric, and sulfuric acids produced by this method contained significantly lower cationic impurities than high-purity acids from commercial sources. A complete system, including the Class 100 environment, production, and storage of these high-purity reagents is described. A method based on spark source mass spectrographic isotope dilution analysis has been developed for the simultaneous determination of 17 elements in these materials. Results of the analyses of both the acids purified by sub-boiling distillation and the ACS reagent grade acids used as starting materials are reported. The sum of the common impurity elements determined in the purified acids ranged from 2.3 ppb in nitric acid to 27 ppb in sulfuric acid. No element in any of the purified acids exceeded 10 ppb and most were well below the 1-ppb level.

The ANALYTICAL CHEMISTRY DIVISION at the National Bureau of Standards has become increasingly involved with the analysis of samples and Standard Reference Materials (SRM's) requiring the determination of elements at the low parts per million (ppm, 10<sup>-6</sup> g/g) to the parts per billion (ppb, 10<sup>-9</sup> g/g) concentration range. This is illustrated by recent analyses which include lead at 3.31 ppm in lunar samples (1), uranium at 72.1 ppb in Trace Elements in Glass (SRM 616) (2), nickel at 1.3 ppm in Orchard Leaves (SRM 1571) (2), and strontium at 0.14 ppm in Bovine Liver (SRM 1577) (2). The low level of these elements puts stringent requirements on the purity of reagents used in the analytical procedure.

Inorganic acid purity is of particular importance because of the relatively large amount of these acids required for sample dissolution and other chemical operations. These procedures can require quantities of acids in excess of ten times the sample weight. To take full advantage of the sensitivity and accuracy of an analytical technique, the reagent blank should be held to no more than a few per cent of the amount being determined. Therefore, the accurate determination of an element near the 1-ppm level will depend on the availability of acids containing no more than 1 ppb of the element.

High-purity inorganic acids have been available for some time from commercial sources. Although these acids are satisfactory for many trace element determinations, they are not always adequate for low level trace work either through a lack of purity or high upper limit specifications. Emission

spectrography (3), the technique usually applied to the analyses of high-purity acids, lacks sensitivity causing upper limits to be set at 1 ppb or higher. The determination of the isotopic composition and concentration of lead in lunar samples can be cited as a recent example. A reagent blank of 340 ng Pb was calculated from the producer's values for lead in commercial high-purity acids and the volume of these acids required to dissolve one gram of lunar rock and separate the lead from other constituents. Since the expected Pb concentration was only a few ppm, the introduction of this quantity of external lead (of a different isotopic composition) would have precluded a reliable determination of the Pb present either as to amount or isotopic composition. Using acids purified by sub-boiling distillation, the total blank was determined to be 5 ng for the actual analysis. Consequently, because of this experience and other problems associated with the determinations of trace metals in a variety of materials, the Analytical Chemistry Division at NBS recently set up facilities for the "in-house" purification, analysis, and distribution of inorganic acids.

Sub-boiling distillation was selected as the method of purification for the inorganic acids. No single purification procedure is capable of removing all classes of impurities from these acids. Since the trace element program at NBS is mainly concerned with trace metals, the technique which appeared to be most efficient in removing metallic or cationic impurities, sub-boiling distillation, was studied. In sub-boiling distillation, infrared radiators vaporize the surface without boiling the liquid in the vaporizer compartment. The vapor is condensed on a tapered cold finger and the distillate is collected in a suitable container. Sub-boiling distillation was selected over conventional or boiling distillation since studies have shown that in the latter method significant contamination of the distillate occurs from creeping of the unreacted liquid and entrainment of particulates in the vapor stream formed during bubble rupture (4). Sub-boiling distillation completely eliminates the entrainment problem since no bubbles are formed. Creeping of unreacted liquid from the vaporizer is minimized by the position of the cold finger type condenser. It should be pointed out that while this is an extremely efficient still for the separation of impurities of low vapor pressure such as metal ions, it offers little purification from impurities of high vapor pressure such as organic matter or many of the anions.

Commercial quartz sub-boiling stills which were designed for the production of high-purity water have been used for the production of high-purity mineral acids of low-level lead content at the Carnegie Institution of Washington (5). Similar sub-boiling quartz stills (Quartz Products Corp., Plainfield, N.J.) were installed at NBS for the production of

(1) L. E. Barnes, B. S. Carpenter, E. L. Garner, J. W. Gramlich, F. C. Kuehner, L. A. Muehlan, E. J. Muenchall, J. R. Moody, L. J. Moore, T. J. Murphy, P. J. Paulsen, K. M. Sappendorf, and W. R. Shields, "Isotopic Abundance Ratios and Concentrations of Selected Elements in Apollo 14 Samples," Proc. Apollo 14 Lunar Sci. Conf., *Greechen, Caspers, Ann. Astro. Suppl.*, **3**, 2, MIT Press, Cambridge, Mass., in press.

(2) Office of Standard Reference Materials, *NBS Spec. Publ.*, **260** (1970).

(3) N. A. Kershner, E. E. Jos, and A. J. Barnard, Jr., *Appl. Spectrosc.*, **25**, 542 (1971).

(4) R. C. Hughes, P. C. Miran, and G. Gunderson, *ANAL. CHEM.*, **43**, 691 (1971), and references cited therein.

(5) K. D. Burthuis and S. R. Hart, *ibid.*, **44**, 432 (1972).

hydrochloric, nitric, perchloric, and sulfuric acids as well as water. An all Teflon (Du Pont) sub-boiling still was designed and constructed at NBS for the production of high-purity hydrofluoric acid.

Efficient purification by the still only partially solves the problem of producing and distributing pure acids. Airborne particulate contamination and container contamination must also be minimized to ensure a high quality product. Airborne particulate contamination can be virtually eliminated by enclosing the still and distillate containers in a Class 100 clean air chamber. Teflon FEP bottles which have been vigorously cleaned with nitric and hydrochloric acids are used as containers for the purified acids and high-purity quartz is used for water.

To evaluate the purity of the acids and water produced by this process, an analytical method based on isotope dilution spark source mass spectrometry (SSMS) was developed. This method has limits of detection as low as 0.01 ppb for common impurity elements. Seventeen elements were determined simultaneously in each of the high-purity acids and water produced by sub-boiling distillation and the ACS grade acids used as starting materials.

#### APPARATUS FOR THE SUB-BOILING DISTILLATION OF HIGH-PURITY ACIDS AND WATER

**Quartz Sub-Boiling Still.** The commercially available sub-boiling still shown in Figure 1 is made of quartz. This type still is used for the production of HCl, HNO<sub>3</sub>, HClO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, and H<sub>2</sub>O. Heating of the liquid being distilled is done by a pair of infrared radiators positioned on both sides of the condenser. These elements, inside quartz tubes, heat the surface of the liquid and evaporate it without causing it to boil. This positioning also serves to heat the walls above the liquid tending to keep them dry which minimizes creep of liquid along the walls between the liquid reservoir and the condensing cold finger. The condenser is tilted downward toward the distillate outlet to allow the condensed liquid to flow to the tip above the outlet. The still is fed by a 6.8 pound bottle of ACS reagent grade acid through a liquid level control which maintains the liquid to just below the overflow height. Approximately 400 to 500 ml of liquid are thus maintained inside the still at all times. A three-way stopcock on the liquid level control is used to drain the still after the consumption of each bottle of ACS reagent grade feed acid. All parts of the liquid feed system are made of Teflon.

**Teflon Sub-Boiling Still.** An all-Teflon (Du Pont) sub-boiling still having all the essential features of the quartz still was designed and constructed for the production of hydrofluoric acid. This still, shown in Figure 2, was fabricated starting with a commercial 2-liter Teflon bottle. The heaters, condenser, acid inlet, and the overflow were inserted into what was originally the bottom of the bottle and the distillate outlet was inserted at the bottle cap. For the heaters, Teflon rods are machined to form 19-mm o.d. closed-end tubes. Heating coils inside glass tubes are then inserted into the heater tubes. The maximum operating temperature of the still is limited by the softening point of the Teflon around the heater. The glass tubing serves to support the heating tube. The cold finger condenser is similarly machined into a 25-mm o.d. tube from solid rod. Both the condenser and heater tubes are threaded at the open ends to fit into conversion fittings which are in turn threaded into tapped holes in the bottom of the bottle. The tapped hole in the condenser fitting is machined at an angle such that the condenser is tilted downward toward the distillate outlet. Because HF and other liquids do not adhere readily to Teflon, the distillate drips off instead of flowing down along the condenser. Therefore, a trough is secured under the condenser to catch the HF and direct it to the distillate outlet. A piece of tubing

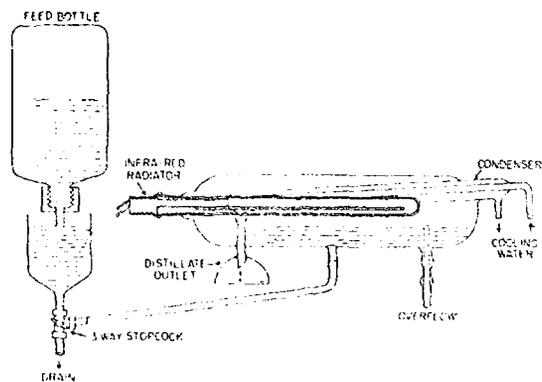


Figure 1. Purequartz sub-boiling still

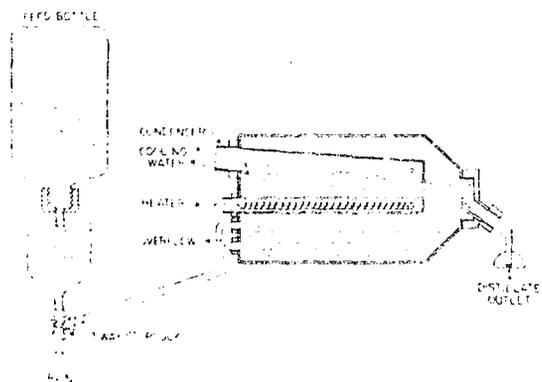


Figure 2. All-Teflon sub-boiling still

inserted through the bottle cap using commercial Teflon fittings serves as a collector for the distillate. The tube is provided with an umbrella at the end to protect the collection bottle from possible fall-out contamination. The acid feed and overflow tubes are attached with Teflon fittings threaded into the bottle bottom. Teflon tape is used when necessary on the threads of the fittings to ensure a liquid tight seal.

**Clean Air Chamber.** Each sub-boiling still is housed in a clean air chamber (Environmental Air Control, Inc., Annandale, Va.) to protect the distillation process from external particulate contamination. All parts on the clean air side of the chamber including the HEPA filter frame and diffuser are constructed of aluminum or plastic. The chambers meet Class 100 specifications—that is, they remove 99.97% of all particulate matter larger than 0.3  $\mu$ m. The air flow through the chamber is adjusted to match the exhaust rate through a plenum assembly at the back-bottom of the unit. By this means, the acid purification operation is protected from room contaminants and at the same time, acid fumes are minimized in the room.

**Containers for Reagent Storage.** Acid distillates are collected and stored in Teflon-FEP bottles. These bottles are cleaned by soaking for 24 hours first in hot 8M HNO<sub>3</sub> and then in hot 6M HCl for 24 hours. They are then rinsed with sub-boiling distilled water and finally with the acid being stored. The containers are reused for the same acid after first being rinsed with distilled water and then rinsed with the acid. Water from the sub-boiling still is stored in quartz containers which are cleaned in the same manner as the Teflon bottles.

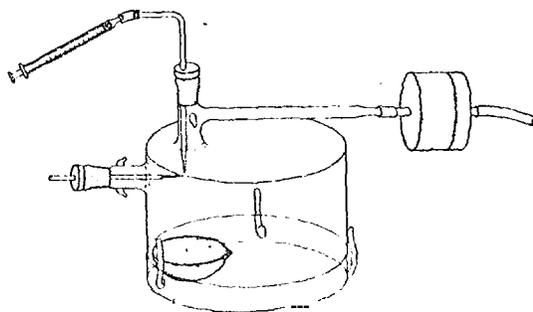


Figure 3. Clean environment evaporator and transfer system

#### APPARATUS AND REAGENTS FOR ANALYSIS OF ACIDS AND WATER

**Enriched Isotope Spike Solutions.** The individual isotopic spikes for the elements being determined were on hand as 1 mg/ml solutions. Compatible spiking elements were combined to give 50  $\mu\text{g/ml}$  concentrations of each element in a pair of master spiking solutions. One solution contained the HCl soluble elements, the other solution the  $\text{HNO}_3$  soluble elements.

**Clean Air Exhaust Hood.** In the analysis of the acids, evaporations were performed on a hot plate in a Class 100 exhausted fume hood. The basic unit is similar to the clean chamber except that the air is exhausted down through a grill of Teflon that serves as a "floor" for the hood and then out through a standard acid fume exhaust system. Teflon is used extensively throughout those parts of the hood exposed to acid fumes.

**Evaporator and Liquid Transfer System.** The apparatus, shown in Figure 3, provides a clean environment for evaporating a spiked sample and transferring the residual volume onto high-purity gold wires. Nitrogen flowing through a 0.1- $\mu\text{m}$  cellulose filter provides a clean atmosphere, sweeps out evaporating acid, and prevents entry of particulate contamination. A pure quartz pipet inserted off center in a Teflon stopper at the top is used to transfer the last few drops of evaporating acid onto pure gold wires positioned from the side joint.

#### PROCEDURE FOR ANALYSIS OF ACIDS AND WATER BY ISOTOPE DILUTION SSMS

The isotope dilution analyses were performed on the acids and water produced by sub-boiling distillation and on the ACS reagent grade acids used as starting materials. In addition, we have also included results obtained in previous analyses of commercial high-purity acids. This variety in the type and source of acids analyzed has resulted in some changes of the procedures used.

**Hydrofluoric Acid.** Due to its reactivity with quartz and glassware, HF was handled exclusively in Teflon-FEP containers, otherwise it was treated the same as the other acids from a similar source.

**Water from the Sub-Boiling Still.** Because the purity of the sub-boiling distilled water was higher than that of the acids, the water was preconcentrated before spiking. Two liters of water were evaporated to approximately 100 ml in the original storage container before being removed and spiked. The water was not spiked in the storage container because of our reluctance to contaminate the container with the enriched spike isotopes. The spiked 100-ml water sample was then handled in the same manner as the acids purified by sub-boiling distillation.

**Sample Spiking.** All samples were spiked using 1  $\mu\text{g/ml}$  solutions freshly diluted from the 50  $\mu\text{g/ml}$  master spike solutions. Acids purified by sub-boiling distillation were all spiked for a nominal concentration of 1 ppb; nitric and hydro-

chloric acids were also spiked for 0.1 ppb. The nominal 1-ppb spike contained 100 ng of each spike element in 100 grams of acid (1 ng/g); the 0.1 ppb spike had 30 ng/300 grams of acid. The 1 ng/g spike gives an altered isotopic ratio of approximately one at a concentration of 1 ppb for most of the impurity elements. Concentrations up to ten times higher and more than ten times lower than the spiked for value can be determined from the measured ratios, but with greater uncertainty.

The ACS reagent grade acids used as starting materials for the sub-boiling distillation were spiked at 1 ppb, 10 ppb, and 100 ppb in order to cover the expected concentration range for the different impurity elements. An element was only measured for the sample where the spike came closest to the actual concentration. One half of the spiked sample was used for each analysis.

The commercial high-purity acids analyzed previously were spiked for many but not all of the elements surveyed in the ACS reagent grade and sub-boiling still acids. One hundred-gram samples were spiked for concentrations in the 1- to 100-ppb range. Because of the higher level of impurities only 20 grams of the 100-gram sample were required for the analyses.

**Sample Evaporation and Transfer to Pure Gold Wires.** The clean environment evaporator shown in Figure 3 was used to vaporize commercial high-purity acids in a standard laboratory fume hood prior to our obtaining a Class 100 clean air fume hood. A single sample at a time was evaporated to a few tenths of a milliliter and then transferred with the pure quartz pipet to the tip of "six nines grade" gold wires and dried.

The ACS reagent grade acids and the acids purified by sub-boiling distillation were evaporated in the Class 100 fume hood in open quartz and/or Teflon beakers on a hot plate. The clean environment evaporation dish was used however to transfer the last few drops of the spiked sample to the gold wires for drying. The gold wires were then heated to 425  $^{\circ}\text{C}$  for 15 minutes to drive off hydrocarbons and occluded acid. At this point partial loss due to incomplete transfer or loss on heating can be ignored inasmuch as the quantitative analytical data are a function of the altered isotopic ratio and the only requirement is that enough of each element be retained for an adequate measurement.

**Spark Source Mass Spectrographic Determination of Altered Isotopic Ratios.** The pair of gold wires was mounted in the spark source such that several millimeters of the wire ends, which were coated with the spiked sample residue, would be overlapping and parallel to each other. When a source vacuum of  $1 \times 10^{-7}$  Torr was reached, a graded series of exposures was made. The electrodes were moved relative to each other during sparking in order to spark new spiked sample residue on each exposure. One half of the surface of each electrode was sampled during this first graded series of exposures. A second identical series of graded exposures was then made on the remainder of the sample. A single photographic plate was used for each sample.

The photographic plates were processed using the bleach and internal image developer for reducing plate fog developed by Cavard (6).

The photoplates were examined visually to select exposures which would give optimum sensitivity for each element determined and for evidence of interferences at the same nominal mass such as unresolved doublets, abnormally wide lines, or isotopic ratios which varied from one exposure to the next. If an interference was indicated for the  $-1$  lines of an element, the less sensitive  $+2$  or  $+3$  lines were considered for measurement. The selected exposures for each element were then densitometered measuring both the spike and natural isotopes on each exposure. From four to six exposures were measured for each element if available.

(6) A. Cavard in "Advances in Mass Spectrometry," E. Kendrick, Ed., The Institute of Petroleum, London, 1968, pp 419-29.

**Calculation of Impurity Concentrations.** The amounts of impurities present in each acid were computed from the sample weight, the weight of each spike added, and the measured altered isotopic ratios using the usual formula for isotopic dilution analysis as described in earlier papers (7, 8). Impurity concentrations were calculated for each isotopic ratio measured for an element. These values were then averaged. This system gives a more realistic evaluation of the uncertainty in the results than using an averaged ratio to calculate one concentration value. This is especially critical when the measured (altered) isotopic ratio is close to that of either the spike or natural element.

When only the spike isotope for an element was detected, an upper limit of concentration was computed by substituting twice the noise level of the photographic plate at the position of the natural isotope for the intensity of the natural isotope. The concentration of mononucleidic sodium was estimated by assuming it has the same sensitivity as potassium and measuring intensity-areas of the  $^{23}\text{Na}$  compared to that of either the  $^{39}\text{K}$  or the  $^{41}\text{K}$  isotope of the same exposure.

The results of these analyses of the acids and water are presented in a later section describing the operating procedure used for the production of each of the acids by sub-boiling distillation.

#### DISCUSSION OF ANALYSIS PROCEDURE

The acids purified in the sub-boiling still and the ACS reagent grade starting materials were analyzed for 17 elements simultaneously by the spark source. The elements measured represent elements found as impurities in reagents, elements commonly determined in many types of analytical samples, and elements from different groups of the periodic table. It was felt that this selection of elements would give a representative view of the overall reagent purity.

The analysis technique itself is subject to blank problems which cannot be properly evaluated. Care was taken during the analysis to prevent contamination of the samples from containers and the external environment. Based upon the lowest values found in repeated analysis of the acids produced by sub-boiling distillation, estimates can be made of the probable blank contributions. In general any element reported near the 0.1-ppb level or below may have a considerable blank contribution and the value should therefore be considered as an upper limit. Concentrations significantly above this level represent actual reagent impurities with uncertainties ranging from  $\pm 10$  to 30% depending on the value of the altered ratio.

Interfering lines having the same nominal mass as either the spike or natural abundance isotope of an element being determined were sometimes encountered during these analyses. These interferences are normally most prevalent for the lower mass elements and for the more impure acids. The three major sources of these lines are hydrocarbons, anions, and anion fragments, and various molecular combinations of the major impurities with themselves and the acid anion. Heating of the sample to 425°C before sparking and the heating that occurs during sparking greatly reduced interference from the hydrocarbon and anion lines.

Examples of anion fragment interferences are  $^{37}\text{Cl}^{16}\text{O}^+$  with the  $^{52}\text{Cr}^+$  spike and  $^{35}\text{Cl}^{16}\text{O}_2^+$  with the  $^{67}\text{Zn}^+$  spike in perchloric acid analysis, and  $^{32}\text{S}^{16}\text{O}_2^+$  with natural  $^{64}\text{Zn}^+$  in sulfuric acid. The perchloric acid interferences can be evaluated by monitoring the line from the other chlorine isotope.

(7) R. Alvarez, P. J. Paulsen, and D. E. Kelleher, *ANAL. CHEM.*, 41, 955 (1969).

(8) P. J. Paulsen, R. Alvarez, and D. E. Kelleher, *Spectrochim. Acta*, 2411, 535 (1969).

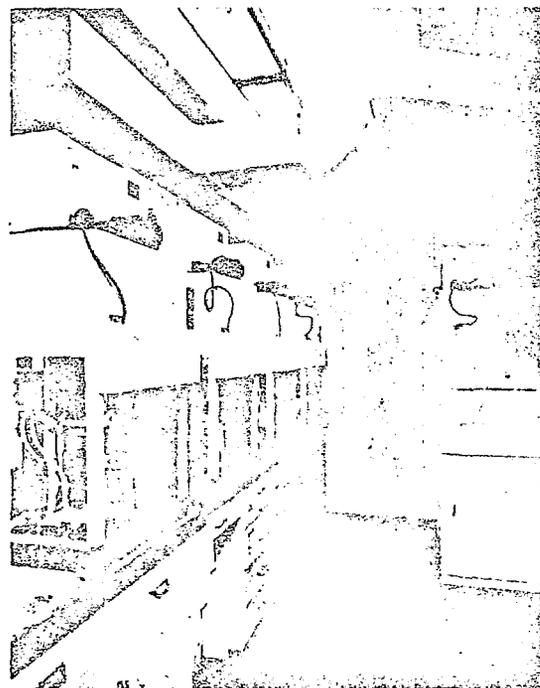


Figure 4. Laboratory for production of high-purity acids

ACS reagent grade  $\text{HClO}_4$  with high levels of Na and K showed lines for:  $\text{NaO}^+$ ,  $\text{NaK}^+$ ,  $\text{Na}_2^+$ ,  $\text{K}_2^+$ ,  $\text{Na}_2\text{Cl}^+$ ,  $\text{K}_2\text{Cl}^+$ ,  $\text{Na}_2\text{ClO}^+$ ,  $\text{K}_2\text{ClO}^+$ ,  $\text{Na}_2\text{ClO}_2^+$ , etc. Some of these lines represented potential interferences; however, this type of interference was not significant for the acids purified by sub-boiling distillation since their cationic impurities were always at a very low level.

Measurement of the isotopic ratio of an element at the  $\pm 2$  or  $\pm 3$  charge state will eliminate all three types of interfering lines since these molecular species fragment rather than form a multiply-charged ion. When such interferences existed, Ag, Cu, and K isotope ratios were measured on  $\pm 2$  ions and Zn, Ni, Cr, and Ca isotope ratios were measured on  $\pm 3$  ions.

#### PRODUCTION AND ANALYSIS OF HIGH-PURITY ACIDS AND WATER

Figure 4 shows the laboratory setup for the production of high-purity acids. Each quartz sub-boiling still and distillate container is housed in a separate Class 100 clean air unit to prevent particulate contamination during distillation. Any extraneous acid vapor produced is exhausted through the balanced plenum assembly which serves four clean air units. The Teflon sub-boiling still is housed in a separate clean air chamber and extraneous acid vapors are exhausted by a standard laboratory hood. The ACS reagent grade acid to be purified is fed to each still from a container just outside the clean air chamber through a liquid level control which maintains the pre-set liquid level. In this manner, acid is constantly fed to the still as distillate is removed. Since impurities are concentrated in the pot liquid, the still is drained after the consumption of each 6- to 8-pound feed bottle.

After distillation, each acid was allowed to stand in its Teflon-FEP container for at least two weeks before analysis to allow for any impurities in or on the container walls to react with the acid.

**Table 1. 1 Hydrochloric Acid**  
Impurity concentrations ppb by wt (ng/g)

|    | Acid from<br>sub-boiling<br>still | ACS reagent<br>grade | Commercial<br>high purity |
|----|-----------------------------------|----------------------|---------------------------|
| Pb | 0.07                              | 0.5                  | <1                        |
| Tl | 0.01                              | 0.1                  |                           |
| Ba | 0.04                              | 2                    |                           |
| Te | 0.01                              | 0.1                  | ...                       |
| Sn | 0.05                              | 0.07                 | <6                        |
| In | 0.01                              | ..                   |                           |
| Cd | 0.02                              | 0.03                 | 0.5                       |
| Ag | 0.03                              | 0.05                 | 0.2                       |
| Sr | 0.01                              | 0.05                 |                           |
| Zn | 0.2                               | 2                    | 4                         |
| Cu | 0.1                               | 4                    | 1                         |
| Ni | 1.2                               | 6                    | 3                         |
| Fe | 3                                 | 20                   | 7                         |
| Cr | 0.3                               | 2                    | 0.3                       |
| Ca | 0.06                              | 7(1                  | 24                        |
| Mg | 0.5                               | 200                  | 10                        |
| Na | 1                                 | 10                   | 20                        |
|    | Σ 6.2 ppb                         | Σ 820 ppb            | Σ 7(1 ppb)                |

**Table II. Nitric Acid**  
Impurity concentrations ppb by wt (ng/g)

|    | Acid from<br>sub-boiling<br>still | ACS reagent<br>grade acid | Commercial<br>high purity |
|----|-----------------------------------|---------------------------|---------------------------|
| Pb | 0.02                              | 0.2                       | 0.3                       |
| Tl | ..                                | 0.2                       |                           |
| Ba | 0.01                              | x                         |                           |
| Te | 0.01                              | 0.1                       |                           |
| Sn | 0.01                              | 0.1                       | 1                         |
| In | 0.01                              | ..                        |                           |
| Cd | 0.01                              | 0.1                       | 0.2                       |
| Ag | 0.1                               | 0.03                      | 0.1                       |
| Sr | 0.01                              | 2                         |                           |
| Se | 0.09                              | 0.2                       |                           |
| Zn | 0.04                              | 4                         | x                         |
| Cu | 0.04                              | 20                        | 4                         |
| Ni | 0.05                              | 20                        | 3                         |
| Fe | 0.3                               | 24                        | 55                        |
| Cr | 0.05                              | 6                         | 130                       |
| Ca | 0.2                               | 30                        | 30                        |
| K  | 0.2                               | 10                        | 11                        |
| Mg | 0.1                               | 13                        |                           |
| Na | 1                                 | 80                        |                           |
|    | Σ 2.3 ppb                         | Σ 220 ppb                 | Σ 240 ppb                 |

The purified acids were then analyzed by the isotope dilution mass spectrometric method described previously. These analyses characterize the acid as delivered to the user rather than as produced, since this is what is of interest to the analyst.

The Teflon-FEP bottles will be used repeatedly over again to contain the same high-purity acid. It is reasoned that the container should become cleaner with use and cause less contamination to future lots of acids. Any acid not used within a few months will be replaced with freshly distilled reagent.

**Hydrochloric Acid.** Hydrochloric acid and water form a constant boiling mixture at 6*N* hydrochloric acid. Initial experiments were with starting acid of this concentration. Further experiments showed that the starting concentration could be increased to 10*N* HCl without causing bubble formation and that the distilled product was also 10*N*. However, concentrated 12*N* acid could not be used because of bubble formation on heating. Apparently, acid of higher

**Table 111. Perchloric Acid**  
Impurity concentrations ppb by wt (ng/g)

|    | Acid from<br>sub-boiling<br>still | ACS reagent<br>grade acid | Commercial<br>pure acid |
|----|-----------------------------------|---------------------------|-------------------------|
| Pb | 0.2                               | 2                         | 16                      |
| Tl | 0.1                               | 0.1                       |                         |
| Ba | 0.1                               | > 1000                    | 10                      |
| Te | 0.05                              | 0.05                      |                         |
| Sn | 0.3                               | 0.3                       | <1                      |
| Cd | 0.05                              | 0.1                       | 4                       |
| Ag | 0.1                               | 0.1                       | 0.5                     |
| Sr | 0.02                              | 14                        |                         |
| Zn | 0.1                               | 7                         | 17                      |
| Cu | 0.1                               | 11                        | 3                       |
| Ni | 0.5                               | 8                         | 0.5                     |
| Fe | 2                                 | 330                       | 10                      |
| Cr | 9                                 | 10                        | 18                      |
| Ca | 0.2                               | 760                       | 7                       |
| K  | 0.6                               | 200                       | 9                       |
| Mg | 0.2                               | 500                       | 4                       |
| Na | 2                                 | 600                       |                         |
|    | Σ 16 ppb                          | Σ 3400 ppb                | Σ 100 ppb               |

concentration than constant boiling 6*N* can be produced because the azeotropic mixture that condenses on the cold finger absorbs HCl from the HCl-rich vapor to reach the concentration of the acid in the pot.

ACS reagent grade hydrochloric acid diluted to 10*N* or 31 weight per cent with high-purity water was used as the feed acid. The still heaters were adjusted to 225 W of power. About 2 liters of 10*N* high-purity hydrochloric acid were produced per day under these conditions.

Table I shows the analysis of the high-purity acid produced by sub-boiling distillation, the starting ACS reagent grade acid, and a lot of commercial high-purity acid. A summation of these impurity elements shows that the sub-boiling distilled acid contained 6.2 ppb, the ACS reagent grade contained 820 ppb, and commercial high-purity 70 ppb. The only element found in the sub-boiling distilled acid at levels higher than 1 ppb was iron at 3 ppb. The other elements were at the sub-ppb level, generally lower than 0.1 ppb.

**Nitric Acid.** The sub-boiling distillation of concentrated 70% ACS reagent grade nitric acid required a low heater temperature to prevent the HNO<sub>3</sub> vapor in the proximity of the heater from disproportionating to form nitrogen dioxide with resulting discoloration of the distillate. Experiments showed that at a heater power setting of 107 W, little or no discoloration of the distillate took place. As a result, only about 500 ml per day of nitric acid was produced. Titration showed the distillate to be 70% HNO<sub>3</sub>, the same concentration as the starting acid.

Table II shows the results of the analysis of the sub-boiling distilled acid, ACS grade starting acid, and a lot of commercial high-purity acid. The totals of the impurity elements determined were 2.3 ppb for the sub-boiling distilled acid, 220 ppb for the ACS starting acid, and 240 ppb for the commercial high-purity acid. The sub-boiling distilled nitric acid was the purest of the acids produced. No element was found at a concentration greater than 1 ppb and only sodium was detected at that level, and this accounts for almost half of the total impurities found. Most elements were in the 0.05- to 0.01-ppb range.

**Perchloric Acid.** Initial experiments on the sub-boiling distillation of concentrated 70% perchloric (HClO<sub>4</sub>·2H<sub>2</sub>O) showed that high heater temperatures caused the perchloric

**Table IV. Sulfuric Acid**  
Impurity concentrations ppb by wt (ng/g)

|    | Acid from sub-boiling still | ACS reagent grade acid |
|----|-----------------------------|------------------------|
| Pb | 0.6                         | 0.5                    |
| Tl | 0.1                         | 0.1                    |
| Ba | 0.3                         | 0.2                    |
| Te | 0.1                         | 0.1                    |
| Sn | 0.2                         | 0.6                    |
| Cd | 0.3                         | 0.2                    |
| Ag | 0.?                         | 0.6                    |
| Sr | 0.3                         | 0.4                    |
| Zn | 0.5                         | 2                      |
| Cu | 0.2                         | 6                      |
| Ni | 0.2                         | 0.5                    |
| Fe | 7                           | 6                      |
| Cr | 0.2                         | 0.2                    |
| Ca | 2                           | 123                    |
| K  | 4                           | 9                      |
| Mg | 2                           | 4                      |
| Na | 9                           | 50                     |
|    | $\Sigma$ 27 ppb             | $\Sigma$ 20' ppb       |

**Table V. Hydrofluoric Acid**  
Impurity concentration ppb by wt (ng/g)

|    | Acid from sub-boiling still | ACS reagent grade acid |
|----|-----------------------------|------------------------|
| f% | 0.05                        | 0.8                    |
| Tl | 0.1                         | 0.2                    |
| Ba | 0.1                         | 0.5                    |
| Te | 0.05                        | 0.1                    |
| Sn | 0.05                        | 11                     |
| Cd | 0.03                        | 2                      |
| Ag | 0.05                        | 0.1                    |
| Sr | 0.1                         | 0.5                    |
| Zn | 0.2                         | 4                      |
| Cu | 0.2                         | 3                      |
| Ni | 0.3                         | 12                     |
| Fe | 0.6                         | 110                    |
| Cr | 5                           | 21                     |
| Ca | 5                           | 14                     |
| K  | 1                           | 28                     |
| Mg | 2                           | 10                     |
| Na | 2                           | 100                    |
|    | $\Sigma$ 17 ppb             | $\Sigma$ 320 ppb       |

acid in the still to turn bright yellow, probably because of the formation of chlorine dioxide. At lower power settings, little or no color was noted and the distillate was colorless. Another problem with this distillation was that in the earlier work, crystals would occasionally build up on the cold finger condenser. This material was probably perchloric acid monohydrate ( $\text{HClO}_4 \cdot \text{H}_2\text{O}$ ) which has a melting point of 50 °C. Crystal formation could be controlled by changing either the flow rate of the condenser water or the heater temperature. However, this problem was noted only in the earlier work. For the last six months, no crystal formation on the cold finger has been noted even when the still is operated continuously for weeks. The power setting used for the production of purified perchloric acid was 240 W, and the production rate was about 600 ml of perchloric acid per day. Titration has shown that the distillate is 70 wt % of  $\text{HClO}_4$ , the same as the starting ACS grade acid.

Table III shows the results of the analyses of the sub-boiling distilled acid, the starting ACS grade acid, and a lot of commercial high-purity acid. The total of the impurity elements found was 16 ppb for the sub-boiling distilled acid, 3100 ppb for the starting acid, and 100 ppb for the commercial high-purity acid. These analyses demonstrate the efficiency of sub-boiling distillation when the concentration of impurity elements in the purified product is compared to the starting acid. The concentration of barium which was greater than 1000 ppb was reduced to 0.1 ppb, a purification factor of greater than 10,000. Another example is calcium which was reduced to 0.2 ppb in the purified acid from 760 ppb in the starting acid, a factor of 3,800. It should also be noted that chromium which was present at 10 ppb in the starting acid was not significantly changed in the purified acid. This is probably due to the fact that chromium can be volatilized from hot perchloric acid solutions as chromyl chloride,  $\text{CrO}_2\text{Cl}_2$ , so little, if any, purification can be expected by sub-boiling distillation. Chromium accounts for over half of the total impurities found in the purified acid.

**Sulfuric Acid.** Initial experiments with the sub-boiling distillation of sulfuric acid showed that, because of the density of  $\text{H}_2\text{SO}_4$ , the acid that condensed on the cold finger tended to drop off before reaching the collection tube. Another problem was that even at the highest power setting, the distillation rate was extremely slow. Modification of the still

**Table VI. Water**  
Impurity concentrations ppb by wt (ng/g)

|    | Water from sub-boiling still |
|----|------------------------------|
| Pb | 0.008                        |
| Tl | 0.01                         |
| Ba | 0.01                         |
| Te | 0.004                        |
| Sn | 0.02                         |
| Cd | 0.005                        |
| Ag | 0.002                        |
| Sr | 0.002                        |
| Zn | 0.04                         |
| Cu | 0.01                         |
| Ni | 0.02                         |
| Fe | 0.05                         |
| Cr | 0.02                         |
| Ca | 0.06                         |
| K  | 0.09                         |
| Mg | 0.09                         |
| Na | 0.06                         |
|    | $\Sigma$ (1.5 ppb)           |

by increasing the angle of incline of the cold finger condenser solved the condensate problem, and the rate of distillation was increased by using a platinum foil reflector around the still. At the maximum power setting of 427 W, the rate of distillation is now about 300 ml per day. Titration has shown that the purified acid is 96 wt %  $\text{H}_2\text{SO}_4$ , the same as the starting ACS grade acid.

Table IV shows the results of the analyses of the sub-boiling distilled acid and the starting sulfuric acid. The total of the impurities found in the starting acid was 200 ppb, the lowest of any of the ACS grade acids, and the purified acid contained 27 ppb, the highest of the purified acids. Sodium was the principal contaminant in the high-purity acid at 9 ppb with iron right behind it at 7 ppb. These two elements account for over half the total impurities found in the purified sulfuric acid.

**Hydrofluoric Acid.** Hydrofluoric acid was purified in the all-Teflon sub-boiling still shown in Figure 2 which was designed and built at NBS. Hydrofluoric acid and water form a constant boiling mixture at 36% HF. Because of the previous experience with hydrochloric acid, the sub-boiling distillation of concentrated 48% HF was attempted. Titration showed that the distilled product was also 48% HF. Ap-

Table VII. Summary of Experimental Conditions for Producing High-Purity Acids and Water by Sub-Boiling Distillation

| Reagent                        | Concentration of still feed acid, % by wt | Still heater power, W | Concentration of distillate, % by wt | Production rate, ml, 24hr |
|--------------------------------|---|-----------------------|--------------------------------------|---------------------------|
| HCl                            | 31  | 225                   | 31                                   | 2,000                     |
| HNO <sub>3</sub>               | 70  | 107                   | 70                                   | 500                       |
| HClO <sub>4</sub>              | 71  | 240                   | 70                                   | 600                       |
| H <sub>2</sub> SO <sub>4</sub> | 96  | 427                   | 96                                   | 300                       |
| HF                             | 48  | 164                   | 48                                   | 300                       |
| H <sub>2</sub> O               |   | 200                   |                                      | 4,000                     |

parently, as in the case of hydrochloric acid, the azeotropic mixture that condenses on the cold finger absorbs HF from the HF rich vapor to reach the same concentration as the acid in the still.

Since the heaters of the Teflon still for the purification of hydrofluoric acid are enclosed in Teflon tubes, the temperature of the heater had to be kept below the softening point of Teflon. As a result the maximum power setting for this still was 164 W which produced a distillation rate of 300 ml per 24 hour day.

Table V shows the results of the analyses of the starting ACS grade HF and the purified product. The total of the impurities in the purified acid is 17 ppb compared to 320 ppb in the starting ACS grade acid. The two principal impurities in the purified acid are Cu and Cr, both at 5 ppb, and they account for over half the total impurity found. The only other elements found at a concentration of greater than 1 ppb are K at 1 ppb, Mg at 2 ppb, and Na at 2 ppb.

**Water.** Water has been included in this study because it is the most commonly used chemical reagent and because sub-boiling distillation has been used to produce high-purity water both here at NBS and elsewhere. Initially, water of higher purity than the distilled water from the laboratory distribu-

tion system was obtained by re-distillation in a commercial, continuous-feed still. This still had a tin-coated evaporator and baffle and was equipped with a quartz condenser. This unit was designed to disengage CO<sub>2</sub> and other gases from the distillate and vent them off. Water produced by this still was used as the feed water to the sub-boiling still. The entire assembly of feed apparatus, quartz sub-boiling still, and quartz collector was contained in a Class 100 clean air chamber. The distillation rate at a power setting of 200 W was 4 liters per day.

The analysis of the sub-boiling purified water is given in Table VI. This water contained a maximum of 0.5 ppb total of the 17 elements determined. No element was detected at a concentration of greater than 0.1 ppb. Since no correction for an analysis blank could be made, the values must be regarded as upper limits for the purity of the water. The water may in fact be more pure than the analysis indicates.

The optimum conditions for the production of each high-purity acid and water by sub-boiling distillation described above are summarized in Table VII.

The impurity elements determined in the acids and water (Tables I-VI) are tabulated in order of decreasing mass. This reveals that the major impurities for the acids purified by sub-boiling distillation are all low mass elements. None of the NBS purified acids have an impurity level as high as 1 ppb for elements above iron in mass. Elements from iron on down sometimes exceed 1 ppb but none exceeded 10 ppb.

A number of the major impurities found in the ACS reagent grade and commercial high-purity acids are elements common to their glass storage containers. It would appear that the means of storing the acids are as responsible for the acid purity as the purification method. It should be noted that of all the acids analyzed, only the ACS grade perchloric acid showed an element (Ba) that exceeded the 1-ppm level.

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