



REGIONAL  
SEAS

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*Reagent and laboratory-ware  
clean-up procedures for  
low-level contaminant monitoring*

*Reference Methods For Marine Pollution Studies No. 65*

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UNEP 1995

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## PREFACE

The Regional Seas Programme was initiated by UNEP in 1974. Since then the Governing Council of UNEP has repeatedly endorsed a regional approach to the control of marine pollution and the management of marine and coastal resources and has requested the development of regional action plans. The Regional Seas Programme at present includes 12 regions and has some 140 coastal States participating in it (1), (2).

One of the basic components of the action plans sponsored by UNEP in the framework of the Regional Seas Programme is the assessment of the state of the marine environment and of its resources and of the sources and trends of the pollution, and the impact of pollution on human health, marine ecosystems and amenities. In order to assist those participating in this activity and to ensure that the data obtained through this assessment can be compared on a world-wide basis and thus contribute to the Global Environment Monitoring System (GEMS) of UNEP, a set of Reference Methods and Guidelines for marine pollution studies is being developed as part of a programme of comprehensive technical support which includes the provision of expert advice, reference methods and materials, training and data quality assurance (3). The methods are recommended to be adopted by Governments participating in the Regional Seas Programme.

The methods and guidelines are prepared in co-operation with the relevant specialized bodies of the United Nations systems as well as other organizations and are tested by a number of experts competent in the field relevant to the methods described.

In the description of the methods and guidelines the style used by the International Organization for Standardization (ISO) is followed as closely as possible.

The methods and guidelines, as published in UNEP's series of Reference Methods for Marine Pollution Studies, are not considered as final. They are planned to be periodically revised taking into account the development of our understanding of the problems, of analytical instrumentation and the actual need of the users. In order to facilitate these revisions the users are invited to convey their comments and suggestions to:

Marine Environmental Studies Laboratory  
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which is responsible for the technical co-ordination of the development, testing and intercalibration of Reference Methods.

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- (1) UNEP: Achievements and planned development of the UNEP's Regional Seas Programme and comparable programmes sponsored by other bodies. UNEP Regional Seas Reports and Studies No. 1, UNEP, 1982.
  - (2) P. HULM: A strategy for the Seas. The Regional Seas Programme: Past and Future, UNEP 1983.
  - (3) UNEP/IAEA/IOC: Reference Methods and Materials: A Programme of comprehensive support for regional and global marine pollution assessments. UNEP, 1990.

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A major problem encountered by monitoring laboratories is the availability of good quality reagents. This Reference Method primarily deals with this problem and describes protocols to purify commonly used solvents and acids. The methods described have proven to be robust and effective within monitoring programmes. Specifications are given for the relevant apparatus (which is commercially available), but the text concentrates on the procedures and the practical problems frequently encountered. Of paramount importance with the methods are the potential dangers involved and attention is drawn to the numerous caution notes which are incorporated.

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## 1. Scope

This compilation describes tested methods for cleaning laboratory ware for trace organic and trace metal analyses as well as methods for purifying water, the organic solvents *n*-hexane, dichloromethane, acetone, acetonitrile, toluene, methanol, and the acids HCl, HNO<sub>3</sub>, HF, HClO<sub>4</sub>.

## 2. References

- American Society for Testing and Materials (ASTM). 1989. ASTM D 4210-89. Standard Practice for Intralaboratory Quality Control. Procedures and a Discussion on Reporting Low Level Data. ASTM, Philadelphia, PA19103. p14-20.
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## 3. Introduction

Analyses at the trace (1-100 µg/g) and ultratrace (<1 µg/g) levels demand high sensitivity, i.e. low detection limits. The detection limit of a given analytical procedure depends, in part, on the sensitivity of the instrument used to generate and measure a compound or element-specific signal. For a signal to be detectable, it must be possible to clearly differentiate it from background noise. Modern analytical instruments, if operated

under conditions specified by the manufacturer, contribute very little to the noise signal. Operator-dependent random variations of the analytical signal usually add more to the noise level. Determination of its magnitude is possible by multiple analyses of the same analyte under constant conditions and statistical treatment of the results. However, there are contributions to the analytical noise which cannot be determined by statistical methods: the material to be analyzed may have become contaminated during the sampling procedure and/or by subsequent manipulations prior to the actual measurement, by material equal to or feigning the substance or substances under investigation. This contribution to the noise level is referred to as the procedural blank. Disregarding the usually minimal instrument contribution to the noise signal, the relationship between the detection limit (D.L.), the procedural blank, and its variability can be described by the simple equation:

$$\text{D.L.} = \bar{x} + k\sigma_{\text{blank}}$$

where:  $\bar{x}$  = average value of the blank,  
k is a constant (usually set at 3),  
 $\sigma_{\text{blank}}$  = standard deviation of the blank.

More recently, and in the context of trace element studies, the limit of detection (L.O.D.) has been defined as the lowest concentration level that is statistically different from a blank at a specified level of confidence (Taylor, 1987; Howard & Statham, 1993; ASTM, 1989). Again, the criterion used is three standard deviations ( $3\sigma$ ) of the blank value. The L.O.D. is then described by the simple equation:

$$\text{L.O.D.} = k\sigma_{\text{blank}}$$

where: k is a constant (usually set at 3),  
 $\sigma_{\text{blank}}$  = standard deviation of the blank.

Consequently, a low procedural blank kept at a constant minimum level is an important prerequisite for achieving high sensitivity. The procedural blank comprises all materials which positively interfere with a given measurement. However, it is not uncommon that unintentional contamination of a sample introduces material which quenches the analytical signal and thus reduces apparent concentrations. The accidental loss of analyte by, e.g., evaporation, adsorption or oxidation, has the same effect. Hence, not only must all substances be excluded which contribute to a positive blank signal, but also those influences which negatively interfere with it. Even if analytical procedures and instruments in present use do not register any such interferences, future more refined versions perhaps will. This aspect is important to remember if part of a sample is to be stored for future reference.

From this short and by no means exhaustive discussion, it follows that all efforts must be made not to introduce extraneous materials during sample collection and work-up, and that any material a sample comes in contact with, be it sampler, glassware, solvents, reagents, etc. have to be of utmost purity.

For a variety of reasons, it may not always be possible to achieve this ultimate goal. Sometimes it is sufficient to attain a level of purity commensurate with the requirements of a specific analytical procedure, but insufficient for other purposes. An example will be given in Section 5.4. (Hexäne).



The work described below requires well ventilated laboratories in order to avoid vapour concentrations in the room air which may pose a health hazard if inhaled, or the risk of explosion if ignited. Laboratories where flammable liquids or acids are to be handled and/or distilled must be equipped with emergency showers, eye wash facilities, and fire extinguishers. Buffered eye wash solution (e.g. Eyesaline®, available through Lab. Safety Supply - see section 9) must be within easy reach (10 seconds and 100 feet of hazards, 10 feet for strong acids/corrosives). The minimum protective clothing is a lab coat. If there is any risk of explosion or implosion, safety glasses or safety goggles must be worn. If aggressive liquids are to be handled such as acetonitrile or acids, appropriate aprons and gloves are as indispensable as eye protection. All safety equipment has to be checked periodically.

Physical constants in the following paragraphs are cited from the Handbook of Chemistry and Physics, 52nd edition (The Chemical Rubber Company, 1971). Additional physical constants and toxicological data were taken from the Handbook of Environmental Data on Organic Chemicals (Verschuere, 1977). Boiling points are quoted for normal atmospheric pressure (101.325 kPa or 1013.25 mbar). Also consulted were appropriate chapters in: Techniques of Chemistry, II. Organic Solvents, 3rd edition (Riddick & Bunger, 1970); Contamination Control in Trace Element Analysis, (Zief & Mitchell, 1976); and Methods of Seawater Analysis (Grasshoff *et al.*, 1983).

## 4. Cleaning of laboratory glassware and/or equipment

### 4.1. For trace organic analyses

The material of choice for analytical equipment used in trace organic analyses is borosilicate glass (Pyrex, Duran, etc.). Soft glass (also called soda-lime glass) is suitable as well, but it breaks more easily under mechanical or heat stress. For special purposes, mainly photochemical investigations, flasks etc. are used made of vitreous silica. It is cleaned by employing the same procedure as described for 'glassware'.

Glassware, if visibly dirty, is first cleaned with a household cleaning powder such as Ajax® or similar, tap water, and a bottle brush followed by copious rinsing with hot tap water. The glassware is then immersed for several hours (overnight) in a dilute aqueous laboratory detergent solution such as Alconox® (available through Aldrich Chemical Company or Cole Parmer Co.), Merz Mucosol® (available through Rudolf Brand GmbH & Co., Roth RBS® (Carl Roth GmbH & Co.), Extran MA® (E. Merck), etc. It should be noted that if organophosphorus compounds are to be analysed, phosphate free detergents (such as Micro®, which is available through Bioblock Scientific) should be used. Small pieces of glassware may be cleaned effectively by ultrasonication for 10 minutes in detergent solution. Following detergent treatment, the glassware is rinsed with abundant hot tap water (10 rinses), organic free ion exchange water (see Section 7), and is then air-dried in a laminar flow hood. To ensure that the quality of tap water is adequate for the purpose, rinses should, for a test, be done with ion exchange water. Regular distilled water may be used instead of organic free ion exchange water, but then the glassware must be heat treated in a clean drying oven at 200 °C or above for several hours. This treatment is also recommended for glassware rinsed with organic free water. It is not recommended for volumetric glassware as its calibration may be

affected. Rinsing with pure organic solvents can be effective (e.g. for volumetric flasks) but has some drawbacks: clean organic solvents are expensive; vapours may pose a health hazard if inhaled; in drying ovens solvent vapours may pyrolyze on hot metal surfaces, and vapours of high boiling pyrolysates may condense on the glassware negating all previous efforts.

An oven for drying cleaned glassware must not be used for any other purposes. Otherwise it may too easily itself become a source of contamination.

Checks must be run at regular intervals to ensure that the chosen cleaning procedure is adequate for a given purpose. This is done by rinsing the cleaned glassware with the amount of solvent/acid used for a given analytical procedure followed by the same work-up and analysis as for the analyte (see Section 5.1).

Because vapours and particles suspended in room air collect on surfaces, it is advisable to clean laboratory glassware shortly before use or to keep it in a laminar flow hood. Aluminum foil, often used for protection from dust and vapours can be a source of contamination, because lubricants used in manufacture may adhere to its surface. Rinsing with solvents such as acetone or hexane and air drying under a fume hood usually removes extraneous material. Even under the cleanest of conditions, safe storage times for glassware and other materials used in analytical procedures are limited and must be determined by periodic checks as outlined in the previous paragraph.

## 4.2. For Trace Metal Analyses

### 4.2.1. Laboratory materials

Trace metal analyses in environmental matrices (especially in seawater) demand extreme precautions to avoid secondary sample contamination. All manipulations must strictly avoid contact of the sample with any metal surfaces, metal vapours, and materials which, under the conditions of sampling, sample storage, sample work-up, and analysis, release metals in quantities sufficient to cause significant blank levels, either in ionic form or uncharged. In addition to obvious candidates, this is also the case for soft- or soda-lime glass. Because of high levels of trace metal impurities, and because its surface acts as an ion exchanger, equipment made of soda-lime glass cannot be used for trace metal analyses. The same applies to borosilicate glass with one exception: laboratory-ware made of borosilicate glass may be used for mercury analyses.

A variety of plastics are used in the construction of laboratory-ware, and careful selection is necessary to minimise interferences in trace metal analyses. A review of the chemical and physical characteristics of materials used in the manufacture of laboratory products has been published in: "Inorganic Trace Analysis: Philosophy and Practice" (Howard & Statham, 1993). This is most valuable in selecting laboratory apparatus for a given analysis. In general, it is best to avoid all coloured plastics as many of the colouring materials are major sources of metals. Blank tests must be made in order to check for possible contamination.

For trace metals other than mercury, low density polyethylene (LDPE) is the recommended material, as it should not be a major source of contaminating metals. Laboratory-ware made of Teflon (PTFE, PFA, FEP), and vitreous silica or fused quartz can also be used. High density polyethylene (HDPE), and polypropylene are less suitable, because

the manufacture of these plastics include catalytic processes involving some trace elements. The risk of contamination may therefore be high.

For mercury, Teflon (PTFE, PFA, FEP) is the material of choice. Quartz or borosilicate glass can also be used. Plastics other than Teflon are not recommended because of adsorption of mercury onto the walls of the containers or because of diffusive losses through the walls.

For additional information on the suitability of laboratory-ware for trace metal analyses see: *Inorganic Trace Analysis: Philosophy and Practice* (Howard & Statham, 1993); and *Methods of Seawater Analysis* (Grasshoff *et al.* 1983).

#### 4.2.2. Cleaning procedure

For trace metal analyses, new or conventionally cleaned apparatus is unsuitable. Almost without exception, a vigorous cleaning procedure is required when a new container is first put into use. The extent and nature of subsequent cleaning depends very much on the application for which the container is to be used. Blank tests must be run to check the efficiency of the chosen cleaning procedure.

The following procedure for cleaning is appropriate for laboratory-ware made of any of the materials described in Section 4.2.1. It involves a degreasing step followed by sequential leaching of the containers with hydrochloric and nitric acids, which have been shown to provide complementary cleaning actions (see: *Inorganic Trace Analysis: Philosophy and Practice*, Howard & Statham, 1993).

Degreasing can normally be achieved using commercial detergents (see Section 4.1). Compatibility of the cleaning materials with both the final analysis and the chemical nature of the container to be cleaned must be considered at this early stage. The laboratory-ware is immersed for several hours (overnight), or for several minutes when using ultrasonication, in a dilute aqueous laboratory detergent solution. Heating the bath to about 60°C enhances the cleaning process. The laboratory-ware is then rinsed with copious quantities of tap water (ten rinses) followed by three rinses with purified distilled or deionized water (see Section 7). A blank test must be run to ensure that the tap water is sufficiently clean. If it is not, purified water has to be used exclusively.

The next step is a treatment with hydrochloric acid (1:1, v/v, analytical reagent grade, diluted with purified water). The laboratory-ware is immersed in the acid solution for one week at room temperature or 3 days at 50°C. It is then rinsed thoroughly (at least three times) with purified water.

The final treatment is immersion in nitric acid (1:1, v/v, analytical reagent grade, diluted with purified water). The laboratory-ware is soaked in the acid for one week at room temperature or 3 days at 50°C. It is then, once again, rinsed thoroughly (at least three times) with purified water.

For certain applications not requiring the stringent cleaning protocols described above, a treatment with 1:1 nitric acid solution followed by a 1:9 nitric acid solution can be sufficient for the cleaning of plastic-ware used for the analysis of trace metals (with the exception of methylmercury, for which HCl cleaning is necessary). Adequacy of the protocol must, however, be checked using procedural blanks.

The laboratory-ware is then air dried in a laminar flow hood, and sealed in polyethylene bags if not for immediate use. Sample containers, i.e. bottles and flasks, should be stored filled with 0.1% ultrapure hydrochloric acid (HCl) or nitric acid (HNO<sub>3</sub>). Teflon bottles for Hg analysis should be tightly closed using pliers.

## 5. Purification of Organic Solvents for trace analyses

In many countries reagents and solvents are commercially available at very high degrees of purity. However, high purity chemicals are expensive so that it may often be advantageous to invest in the equipment needed for purification. Whether or not it is wise to spend the money on apparatus and labour necessary for purification depends on a number of variables such as:

- the amount of reagent or solvent required per unit time,
- the cost and purity of the inferior quality starting material,
- the cost of labour, energy, cooling water, maintenance, etc.,
- the price of the purification equipment.

For example, spectrograde *n*-hexane (Merck Uvasol) in Germany is DM 169 per lot of 2.5 liters or DM 67.60 per liter, whereas the price of a 25 liters drum of pure (at least 97%) hexane (Hexane reinst) is DM 387.50 or DM 15.50 per liter (prices quoted from 1992/93 Merck catalogue). Thus, if 25 liters of pure hexane could be further purified to spectrograde quality without any additional cost and without losses, the saving would be DM 1302.50. Reducing this sum by 25% (all ancillary costs and unavoidable losses during purification) leaves a net saving of DM 976.86 per 25 liters. Assuming that 100 liters of spectrograde hexane are needed, the savings are DM 3907.50. Making the further reasonable assumption that this is the approximate price of a fairly sophisticated distillation apparatus, the equipment will start saving money as soon as the volume of purified *n*-hexane exceeds that volume. This calculation is, of course, merely an example to draw attention to the considerations. Any specific calculation must be based on local conditions.

### 5.1. Blank determinations

Solvents have to be checked for impurities routinely, even after most careful distillation. Because most analytical procedures involve solvent concentration, blanks have to be determined in equivalent concentrates employing the same detection system as used for sample analysis. Thus, for example, the fluorescence blank value has to be determined for hexane to be used as water extractant for UV spectrofluorimetric determinations of dissolved oil residues including, if appropriate, concentration by evaporation. A satisfactory blank for capillary gas chromatography with electron capture detection is usually the most difficult to achieve.

The procedural blank is different from the solvent blank. For its determination the solvent has to be taken through the entire analytical procedure including drying, transfers, concentration, etc. It should be determined after the solvent blank.

## 5.2. Cleaning of distillation columns

Even the best of solvent stills is worthless if contaminated. Eventual contamination of a still used for solvent distillation is unavoidable. The degree of contamination depends upon the purity of the starting material and the volume processed. An effective cleaning procedure for a distillation column contaminated with high boiling organic residues is refluxing concentrated nitric acid through it for several hours. After cooling and after most of the acid adhering to the column fillings and other surfaces has dripped back into the sump, the acid in the boiling flask is replaced with organic free ion exchange water (see Section 7). Refluxing is resumed to remove remaining acid from the distillation column. This treatment has to be repeated until the water remains neutral. The column then is left to dry. Drying can be accelerated by distilling some ultrapure methanol through it. This procedure has to be repeated when blank determinations (see 5.1. above) indicate declining product quality.

## 5.3. Distillation "heads" and "tails"

Distillation "heads" (components of a mixture with lower boiling points than the clean product) and "tails" (material boiling at higher temperatures, i.e. remaining in the sump) must be collected in unbreakable containers separately for halogen-free and halogenated organic solvents and must be disposed of following local legislation. Light ends may sometimes be used for rinsing apparatus. An appropriate blank determination must show that this is possible.

## 5.4. Hexane (I).

Molecular weight: 86.17 Daltons

Boiling point: 68.95 °C

Melting point: -95 °C

Density: 0.6603 <sup>20</sup><sub>4</sub>

Refractive index: 1.37506<sup>20</sup>

Vapour pressure at 20 °C: 15.999 kPa (120 torr); at 30 °C: 25.331 kPa (190 torr)

**Caution:** Hexane is highly flammable. It may be irritating to the respiratory tract and acts as a narcotic at high concentrations. The no effects level for man is 2000 ppm (7160 mg/m<sup>3</sup>). Dizziness occurs at 5000 ppm (17900 mg/m<sup>3</sup>). The lethal concentration in air for mice is approximately 40000 ppm (143 200 mg/m<sup>3</sup>).

The one step distillation procedure described below will furnish a product with acceptable UV-F blank values at 310 nm excitation and 320 to 500 nm emission wavelength. It is not suitable, however, for synchronous excitation spectrofluorimetry nor is it sufficiently pure to qualify as solvent for gas chromatography with flame ionization detection (GC/FID) and even less so for gas chromatography with electron capture detection (ECD). Repeated distillation does not improve the quality of the product. Preparation of hexane meeting the more exacting standards required by these analytical methods are described in Section 5.5. (Hexane II). The distillation apparatus for this first uncomplicated protocol is relatively simple (Fig. 1) and is available at a price much below the figure quoted in Section 5.

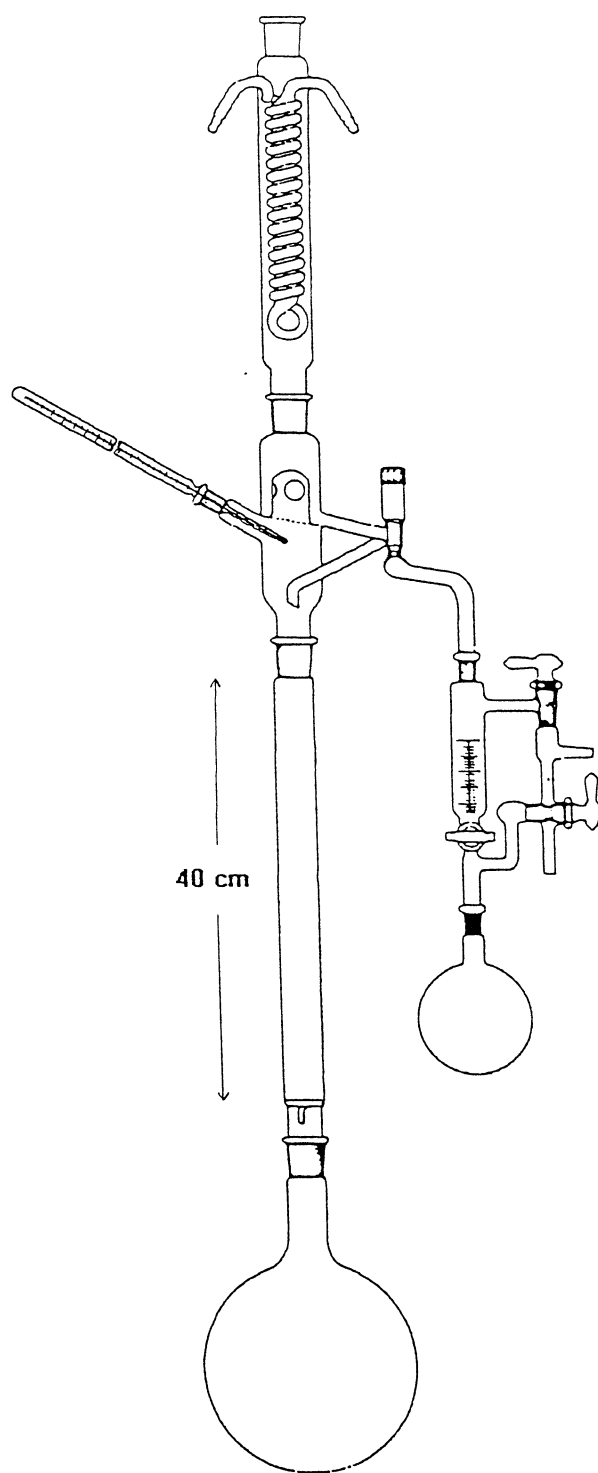


Figure 1. Distillation apparatus for organic solvents  
(as described in Section 5.4.)

#### 5.4.1. Equipment

All-glass distillation apparatus (see Fig. 1) consisting of:

- 2 liters or larger round bottom flask with spherically ground neck, preferably  $\text{\textasciitilde}$  29,
- heating mantle,
- fractionation column, at least 40 cm, preferably vacuum-jacketed to protect against heat loss, and filled with 6 mm diameter glass helices (affording approximately 15 theoretical plates)
- mechanically variable reflux ratio distillation head
- thermometer
- reflux condenser
- adapter
- at least two receiving flasks
- two molecular sieve traps.

#### 5.4.2. Chemicals

- Hexane fraction, ACS reagent or equivalent
- pre-combusted (500 °C, 24 hours) sodium sulphate
- molecular sieve 50 nm, 10 mesh ASTM
- boiling chips.

Note: the 50 nm molecular sieve traps (which are fitted to the top of the reflux condenser and at the side tube of the adapter for the receiving flask) serve to prevent vapours in the outside atmosphere to reach the interior of the distillation apparatus.

#### 5.4.3. Procedure

With high ambient air temperatures and humidity, as encountered in many tropical countries, the feedstock hexane may dissolve sufficient amounts of water so that a binary azeotrope is formed, i.e. a mixture with a lower boiling point than those of its individual constituents (composition = 94.4% *n*-hexane, 5.6% water, b.p. 61.6 °C). Upon condensation, the azeotrope will separate into two phases. If this happens, the hexane has to be dried with sodium sulphate before distillation. During the initial phase of distillation, all of the condensed distillate is refluxed until in the fractionation column ascending vapour and descending liquid phase are in equilibrium, i.e. the head thermometer shows constant temperature, usually well below the boiling point of the pure product. It is useful to remember that boiling temperatures are positively correlated with atmospheric pressure. After equilibration, the reflux ratio is adjusted 1/20, i.e. 5% product is collected of the condensed vapour, 95% are refluxed. The fore-runings, in the order of 10% of the raw material, are collected separately until the head thermometer indicates the boiling point of the pure product. The distillation light ends may be used for rinsing aluminum foil and/or small pieces of glassware such as flasks, if a blank test confirms that impurities are removed rather than added.

**Caution:** Do not dry solvent rinsed equipment in an oven (see Section 4.1).

## 5.5. Hexane (II)

The product of the following procedure has been tested repeatedly to meet the most stringent standards of purity. The distillation apparatus is shown in Fig. 2.

### 5.5.1. Equipment

All-glass distillation apparatus (see Fig. 2) consisting of:

- 6 liters round-bottom flask with spherically ground  $\text{F } 35/25$  socket in short central neck and two side tubes with  $\text{F } 19$ ,
- Electric heating mantle,
- 160 cm vacuum-jacketed and silver-plated distillation column filled with glass helices (approximately 25 theoretical plates),
- magnetically operated, product divider type, adjustable reflux ratio distillation head with reflux condenser,
- heating and reflux ratio control unit,
- product cooler,
- water cooled receiver with bottom drain (Teflon stopcock),
- sump thermometer,
- product thermometer,
- contact thermometer for limiting maximum product boiling point,
- compressed high purity nitrogen in steel tank,
- nitrogen regulator,
- $\text{F } 19$  connecting tube,
- 1/4" Teflon tubing,
- 1/8" Teflon tubing,
- bubble counter,
- two molecular sieve traps.

### 5.5.2. Chemicals

- Hexane fraction, ACS reagent or equivalent
- 50 nm molecular sieve, 10 mesh ASTM
- boiling chips
- ultrapure nitrogen in pressure tank
- concentrated phosphoric acid

### 5.5.3. Preparation

The distillation apparatus (Fig. 2) is equipped with molecular sieve traps on top of the reflux condenser and at the side tube of the receiver. One of the side necks of the boiling flask is connected, *via* the  $\text{F } 19$  connecting tube, 1/8" Teflon tubing, the bubble counter, and the pressure regulator, with the nitrogen tank. The bubble counter, filled with some concentrated phosphoric acid, serves to indicate a slow flow of nitrogen through the apparatus which escapes through the molecular sieve traps.



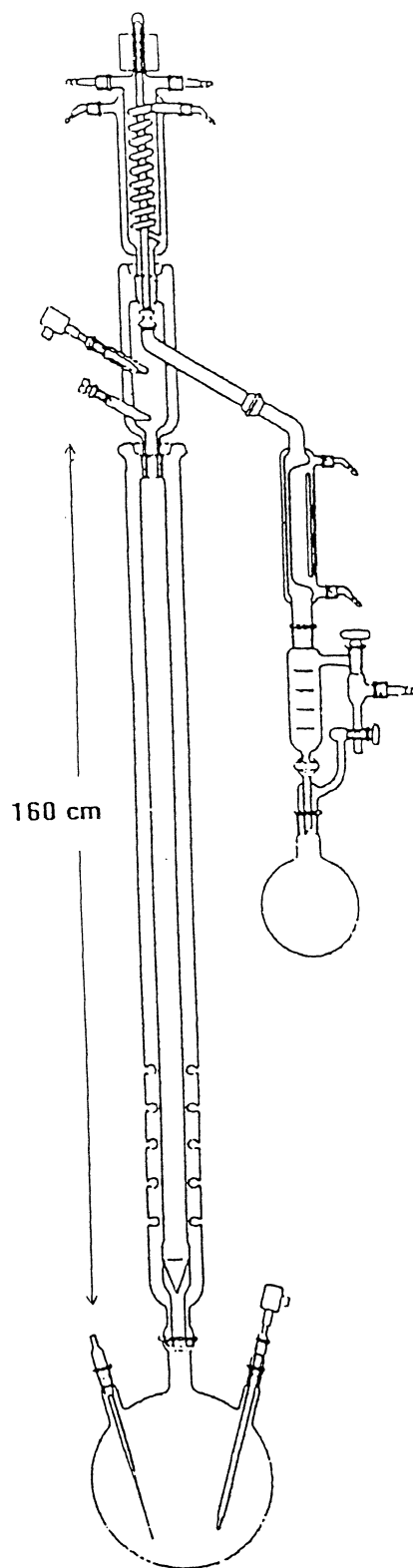


Figure 2. Distillation apparatus for organic solvents  
(as described in Section 5.5.)

#### 5.5.4. Procedure

Hexane is siphoned from the shipping container, usually a steel drum, into the boiling flask using 1/4" Teflon tubing. Some boiling chips are added, and the heat is switched on, while nitrogen is vented through the distillation apparatus at a rate of a few ml/min. The distillation then follows the procedure described in Section 5.4.3. (Hexane I). The main fraction representing the first distillate is drained from the receiver into clean amber reagent bottles with Teflon-lined screw caps. After collection of a sufficient volume of distillate and when a rapidly rising sump temperature indicates depletion of the pure product, the distillation is terminated. The less volatile residue is drained from the boiling flask which is rinsed and then filled with the first distillate. Fresh boiling chips are added, and the distillation is repeated once for further purification of the product. If a solvent blank determination still shows impurities, the likely reason is contamination of the distillation column. It has to be cleaned as described in Section 5.2. For collection and disposal of distillation "heads" and "tails", see Section 5.3.

#### 5.5.5. Sulphuric acid treatment

Hexane sometimes contains aromatic impurities which can create problems, especially if the hexane is to be used as solvent for gas chromatography with electron capture detection (ECD). Although hexane prepared according to the procedure outlined in the preceding paragraph (Section 5.5.4.) has routinely been found to contain extremely small concentrations of ECD active impurities, sulphuric acid treatment may be necessary depending upon the quality of feedstock and the effectiveness of the distillation apparatus. In contact with concentrated sulphuric acid, aromatic compounds are transformed into their sulphonic acid derivatives by substitution of an H atom with the  $\text{SO}_3\text{H}$  group. The sulphonic acids are water soluble and thus easy to separate from hexane.

**Caution:** Concentrated sulphuric acid is extremely aggressive. The person to carry out the following manipulations has to wear goggles and an apron of acid resistant material. Wearing gloves is not recommended as they tend to become slippery when wet. Skin accidentally wetted with concentrated sulphuric acid must be washed immediately with copious amounts of tap water and neutralized with soap. If sulphuric acid is to be diluted, never add water, but always pour the acid into a large excess of water. The mixing heat is considerable and may cause the acid/water mixture to boil.

To effect sulphonation, the raw hexane is vigorously shaken in a separatory funnel with approximately 1/100 of its volume of concentrated sulphuric acid. As the reaction will warm the hexane, and thus increase its vapour pressure, the separatory funnel after the first few seconds of shaking, has to be turned upside down and vented carefully through its stopcock. After closing the stopcock, shaking is resumed and continued for several minutes with frequent intermittent venting. The separatory funnel is then placed into a metal ring and the dark coloured acid phase allowed to separate from the hexane. After draining the acid, the hexane is washed neutral with organic free ion exchange water (see Section 7) and dried over anhydrous calcium chloride ( $\text{CaCl}_2$ ) or sodium sulphate ( $\text{Na}_2\text{SO}_4$ ) before distillation.

## 5.6. Toluene

Molecular weight: 92.15 Daltons

Boiling point: 110.6 °C

Melting point: -95 °C

Density: 0.8669 <sup>20</sup><sub>4</sub>

Refractive index: 1.4961<sup>20</sup>

UV:  $\lambda^{ab}$  207nm ( $\epsilon = 3.97$ ) 260nm ( $\epsilon = 2.48$ )

Vapour pressure at 20 °C: 2.933 kPa (22 torr); at 31.8 °C: 5.333 kPa (40 torr)

Whenever possible, toluene should be used instead of benzene as an aromatic solvent. In contrast to benzene, toluene is not a pre-carcinogen due to the different mode of its mammalian metabolism. Whereas microsomal mixed function oxidase (MFO) transforms benzene into the carcinogenic arene oxide, metabolism of toluene involves side chain oxidation to benzyl alcohol which is excreted after conjugation with glucuronic acid. However, the acute toxicity of toluene is similar to that of benzene. Concentrations in air >100 ppm (383 mg/m<sup>3</sup>) are unsatisfactory (benzene: 50 ppm), symptoms of illness appear at 300 ppm or 1149 mg/m<sup>3</sup> (benzene: 500 ppm), severe toxic effects have been observed at exposure to 1000 ppm (383 mg/m<sup>3</sup>) for 60 minutes (benzene: 1500 ppm for 60 minutes). The inhalation LC<sub>50</sub> for mice is 5320 ppm (8 hours exposure time). Although the vapour pressure of toluene at 30 °C is approximately 1/3 that of benzene, adequate ventilation of working areas is specially important at elevated ambient temperatures.

### 5.6.1. Equipment

The distillation apparatus for purifying toluene is the same as that described under Section 5.5.1. (Hexane II). The distillation head contact thermometer has to be adjusted for the maximum product boiling point.

### 5.6.2. Chemicals

Toluene: extra pure

50 nm molecular sieve, 10 mesh ASTM

boiling chips

ultrapure nitrogen in pressure tank

concentrated phosphoric acid

### 5.6.3. Procedure

The distillation procedure is the same as described in Section 5.5.4.

## 5.7. Methanol

Molecular weight: 32.04 Daltons

Boiling point: 64.96 °C

Melting point: -93.9 °C

Density: 0.7914 <sup>20</sup><sub>4</sub>

Refractive index: 1.3288<sup>20</sup>

UV:  $\lambda_{\text{gas}}$  183.3nm ( $\epsilon = 2.18$ )

Vapour pressure at 20 °C: 12.266 kPa (92 torr); at 30 °C: 21.331 kPa (160 torr)

**Caution: methanol is absorbed through the skin. The average lethal dose for man (ingestion) is 50-75 g, but human mortality has been observed with doses as low as 11.5 g. Concentrations in air of >200 ppm (256 mg/m<sup>3</sup>) are unsatisfactory. Symptoms of illness are observed at >500 ppm (640 mg/m<sup>3</sup>), and severe toxic effects occur at 2000 ppm (2560 mg/m<sup>3</sup>).**

Methanol is a useful eluant for High Performance Liquid Chromatography (HPLC) because of its high polarity. In addition, the short wavelength position of its UV absorption maximum reduces interference with detection of eluted substances by their UV absorption. However, the vacuum UV absorption maximum of methanol tails to 250 nm (95% transmission) and is approximately 50% at 220 nm (1 cm cuvette; reference: water).

### 5.7.1. Equipment

Extra pure methanol, the usual feedstock for purification by distillation, contains traces of impurities which absorb light energy at wavelength up to 400 nm (transmission at 300 nm is approximately 90%, and around 70% at 250 nm). Most of this material can be removed by one distillation through the simple still described in Section 5.4.1. UV absorption of the distillate starts at approximately 300 nm and is <5% at 250 nm. Distillation using the more elaborate apparatus described in Section 5.5.1. does not improve the quality of the product.

## 5.8. Dichloromethane

Molecular weight: 84.93 Daltons

Boiling point: 40.1 °C

Melting point: -95.1 °C

Density: 1.3266 <sup>20</sup><sub>4</sub>

Refractive index: 1.4242<sup>20</sup>

UV:  $\lambda_{\text{vapour}} < 200$  nm

Vapour pressure at 20 °C: 46.53 kPa (349 torr); at 30 °C: 66.661 kPa (500 torr)

**Caution. Dichloromethane vapours must not be inhaled. The inhalation LD 50 for mice is 15000 ppm (52950 mg/m<sup>3</sup>) at 8 hours exposure time. Concentrations above 400 ppm (1412 mg/m<sup>3</sup>) are disagreeable for man and can cause toxic effects.**

### 5.8.1. Equipment

High purity dichloromethane can be obtained using the same type of distillation apparatus as described in Section 5.5. (Hexane II). However, in subtropical and tropical countries the tap water temperature may become too high to effectively condense dichloromethane vapours. If this problem arises, the cooling water for the condensers and the receiver have to be chilled in a refrigerated circulator bath. A still which is used to purify solvents for ECD work should not be used for also purifying halogenated solvents such as dichloromethane. There is a considerable risk of cross-contamination.

### 5.8.2. Procedure

The procedure for cleaning dichloromethane is the same as described in Section 5.5.4. (Hexane II). Distillation heads and tails have to be stored in containers for halogenated compounds.

## 5.9. Acetone

Molecular weight: 58.08 Daltons

Boiling point: 56.2 °C

Melting point: -95.35 °C

Density: 0.7899 <sup>20</sup><sub>4</sub>

Refractive index: 1.3588 <sup>20</sup>

UV:  $\lambda_{\max}$  near 280nm, tail to 340nm,  $\epsilon \approx 14$

Vapour pressure at 5 °C: 11.866 kPa (89 torr); at 30 °C: 35.997 kPa (270 torr)

**Caution.** Repeated exposure to concentrations between 60 and 2200 mg/m<sup>3</sup> causes chronic conjunctivitis, pharyngitis, bronchitis, gastritis, and gastroduodenitis in man. Severe toxic effects must be expected at and above 9650 mg/m<sup>3</sup> and 60 minutes exposure time.

Equipment and procedure for purifying acetone are the same as described in Section 5.5. (Hexane II). It is important to keep the wall temperature of the boiling flask below 20 °C above the boiling point of pure acetone, otherwise 4-hydroxy-4-methylpentanone-2 will be formed. This product of base, as well as acid catalyzed aldol addition, is a common impurity of acetone. Although it can be removed by careful distillation, traces of it will reappear after prolonged storage. It forms readily in contact with silica gel or alumina.

Distillation will not remove all traces of water from acetone, because it forms an azeotropic mixture containing 1.3% water. If a dry product is required, once distilled acetone should be percolated through a column containing beads of 40 nm molecular sieve before redistillation.

## 5.10. Acetonitrile

Molecular weight: 41.05 Daltons

Boiling point: 81.6 °C

Melting point: -45.72 °C

Density: 0.7857 <sup>20</sup><sub>4</sub>

Refractive index: 1.34423 <sup>20</sup>

UV:  $\lambda_{\text{max}}^{\text{dil}}$  274nm

Vapour pressure at 20 °C: 9.866 kPa (74 torr); at 30 °C: 15.332 kPa (115 torr)

**Caution.** Inhalation of vapours and contact with the skin must be avoided, as acetonitrile is rather toxic. The inhalation LC<sub>50</sub> (8 hours exposure time) for rats is 12800 mg/m<sup>3</sup>. For man, no specific response was observed at 273 mg/m<sup>3</sup> with 4 hours exposure time.

Equipment and procedure for purifying acetonitrile are the same as described in Section 5.5. (Hexane II). Acetonitrile forms an azeotropic mixture with water containing 16.3% water (b.p.: 76.5 °C). Most of the water can be removed by azeotropic distillation with a third component, e.g. ethanol. The ternary azeotrope, acetonitrile (44.0%)/ethanol (55.0%)/water (1.0%) boils at 72.9 °C, followed by the binary azeotrope, acetonitrile (43.0%)/ethanol (57.0%), also boiling at 72.9 °C. This method is advisable, however, only if ethanol is available at low cost, because a relatively large volume is needed for removal of a small amount of water. Another simple method is treatment with activated alumina or silica gel. Treatment with calcium hydride (CaH<sub>2</sub>) and distillation over phosphorus pentoxide (P<sub>2</sub>O<sub>5</sub>) effects further dehydration. Distillation over P<sub>2</sub>O<sub>5</sub> often leads to the formation of an orange colored polymer. If this occurs, the distillation has to be repeated until the colour disappears.

**Caution.** Raw acetonitrile of very poor quality should not be distilled, because there is the hazard of explosive polymerization.

## 6. Solvent storage

Solvents to be used in a laboratory with reasonably clean ambient air should be stored in amber glass reagent bottles with Teflon lined screw caps in a well ventilated and cool storage room. Bottles with ground glass stoppers are not recommended as they tend to "breathe" with changing atmospheric pressure and ambient temperature. Exposure of solvent bottles to direct sunlight must be avoided in order not to raise the temperature and, consequently, the vapour pressure of solvents inside. **Photochemical reactions may occur in bottles made of uncoloured glass, especially with dichloromethane which forms highly toxic carbonyl dichloride (phosgene, COCl<sub>2</sub>).**

Opening of a reagent bottle and transfer of some of its contents replaces at least an equivalent volume of the air inside with ambient air which, especially onboard a ship, may contain diverse vapours. For organic trace analyses in a shipboard laboratory it has been found expedient, therefore, to store small volumes of solvents, as they are needed for a given

purpose, in separate containers. These may be bottles of the type described above. For extreme trace analyses, the solvent is drained from the receiver, into clean 200 ml thick walled glass ampoules with a round bottom. The ampoules filled to approximately three quarters of their capacity, are chilled in liquid nitrogen, flame sealed, and stored upright in boxes with properly profiled hard-foam inserts.

## 7. Purification of water

Analytical work is hardly possible without the use of water as solvent and/or diluent for samples and reagents. No single water supply is appropriate for all analytical applications. The major criterion for the selection of a suitable purification system is to obtain a low reagent blank. The concentration of the analyte in the purified water should be measured and its contribution to the reagent blank calculated.

For the preparation of high quality water, at least two steps are generally necessary. Preliminary purification by reverse osmosis, distillation or ion-exchange is followed by a second step which may be, for example, a second distillation or further ion-exchange. It is normally better to employ two stages which work on different principles than to duplicate one purification technique. Materials used in the construction of the purification apparatus should, clearly, not contain the elements or compounds which are to be determined.

Water used in inorganic trace analyses should be devoid of all cations and anions except  $H^+$  and  $OH^-$ . A general indication of water purity can be obtained by the measurement of its conductivity. However, conductivity is only a gross indicator of the dissolved ionic impurities in the water and cannot be taken as a guarantee of purity for a particular application. The range of conductivity to be expected for source and purified waters is from  $500 \mu S.cm^{-1}$  (or resistivity of  $0.002 M\Omega.cm$ ) for hard tap water, to  $0.05 \mu S.cm^{-1}$  (or  $20 M\Omega.cm$ ) for a very high purity water. Measurement of conductivity can be carried out either using an in-line cell or with a bench apparatus.

### 7.1. Distillation methods

Distillation is an effective method to purify water, but it is a costly consumer of electricity and cooling water. If the still is fed directly from the mains in hard water areas, the formation of deposits will result in a drop in efficiency with time, and frequent descaling will be necessary.

Materials used in the construction of the distillation apparatus have important consequences on the quality of the product. There is little to be achieved by using high purity materials for the construction of stills which are used for the preliminary purification of a raw water. For the purification of water for low level trace metal analyses, however, the still should be constructed from materials such as silica and PTFE, and submerged metallic heating elements must be avoided.

Conventional distillation by boiling significantly reduces the contaminant load of a raw feedstock, but the level of purity which can be attained is highly dependent on still design and operation. The main drawback of this distillation method is that aerosol formation by the boiling process leads to droplets of unpurified material being carried over with the distillate. To minimize this effect, the boiling should be as smooth as possible and an efficient trap for droplets should be provided (i.e. a long and/or tortuous path between the boiler and receiver). The use of two stills in series significantly improves the quality of the final distillate.

Sub-boiling distillation offers a higher purity product. The advantage of this method derives from the fact that distillation of the solution occurs without the formation of spray or droplets which can contaminate the condensate. Distillation rates are, however, much slower than those associated with conventional distillation. Typical sub-boiling distillation units are described in Section 8.2.

Water to be used for organic trace analyses may also be purified by simple distillation over alkaline potassium permanganate. A splash guard should be used or a short column to avoid contamination of the distillate by bursting bubbles. Depending upon its purity, approximately 10 pellets of solid sodium or potassium hydroxide and 1 gram potassium permanganate are added per liter of ordinary tap water. The water is refluxed for an hour to oxidize organic contaminants prior to slow distillation into a clean receptacle (see Section 4.1).

## 7.2. Reverse osmosis

This method involves the separation of dissolved (and particulate) contaminants from water by the application of pressure to force raw water through a membrane, against osmotic pressure. It is a very efficient method as a preliminary purification, especially in areas where the tap water contains high levels of total dissolved solids. Its main advantages are that it can be used continuously with little maintenance, and it is not energy intensive.

Different systems of prefiltration by reverse osmosis are commercially available as ready to use units. For example, the "Milli-RO"® (Millipore Corporation) system, comprises a filtering pack containing a prefilter for the elimination of particles (which also reduces contamination from organic materials), and an osmosis cartridge. This provides good quality water for general use in the laboratory (conductivity 25-10  $\mu\text{S}\cdot\text{cm}^{-1}$ ; resistivity 0.04-0.1  $\text{M}\Omega\cdot\text{cm}$ ). The system has an integral water quality sensor to indicate when a change of cartridge is necessary. Similar systems are made by other manufacturers including: "Prima"® (Elgastat) and "ROpure ST"® (Barnstead).

## 7.3. Ion-exchange

Inorganic trace analyses demand removal of all cations and anions except  $\text{H}^+$  and  $\text{OH}^-$ . This is accomplished effectively with a combination of cation and anion exchange resins. These swap charged contaminants for hydrogen and hydroxyl ions, resulting in the substitution of the contaminant salts by water. It is an effective means of removing a wide range of charged contaminants and is relatively inexpensive to install and simple to operate. In 'hard'



water areas the resin lifetime is short and frequent regeneration may be necessary; so the system can be rather expensive to operate. The technique is therefore best employed as a secondary purification method, following, for example, reverse osmosis.

In order to achieve purification of the water it is necessary to employ both anion- and cation-exchange systems. It is possible to use cation- and anion- resin beds in series, although leakage of ions from each resin results in the water containing residual salts. This problem can be overcome by mixing the cation- and anion- exchangers together to give a mixed bed system.

Once ion-exchange resins have reached their capacity, they can be regenerated: the anion-exchange resin with dilute sodium hydroxide and the cation exchanger with dilute hydrochloric acid. The situation is more difficult with mixed bed systems, as the two systems are intimately mixed and cannot be regenerated with a common reagent. It is recommended that in this case the cartridge is returned to the manufacturer for regeneration/replacement.

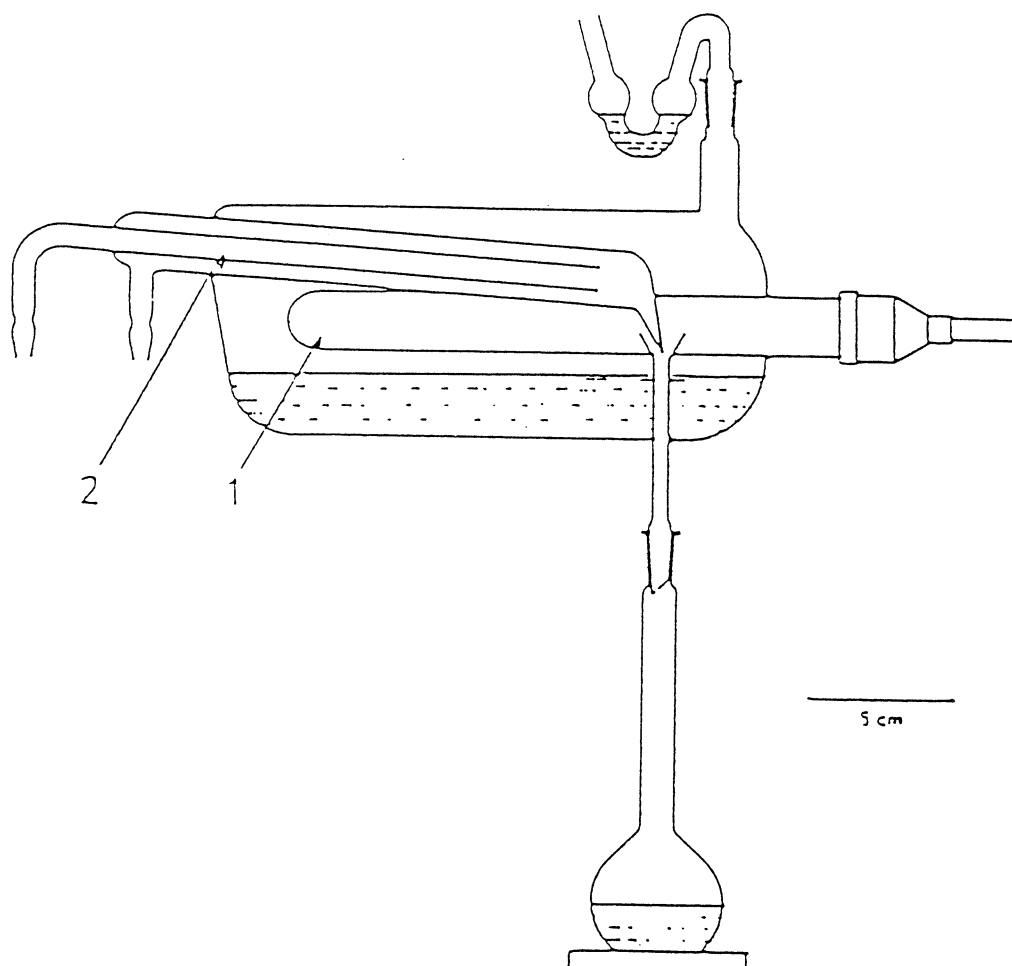
Ion-exchange cartridges can be bought individually from many manufacturers and used alone or in sequence (e.g. Ion-X-changer® filter cartridges, Cole-Parmer Instrument Co.). Also, purifying packs with pre-filtration and mixed-bed resins are commercially available. They are designed to be used as a secondary purification methods. For example, the Milli-Q® Plus water purification system (of the Millipore Corporation, USA) has, in addition to two mixed-bed ion exchanger cartridges, an activated charcoal filter, a cartridge filled with Organex® scavenger resin, and a 0.22 µm filter membrane. This system produces highly purified water (conductivity 0.056 µS.cm<sup>-1</sup>, resistivity 18.2 MΩ.cm; total organic carbon concentration <10 ppb) which is suitable for analyses of both trace metals and organics. The system has an in-line resistivity meter to monitor the quality of the purified water. Similar systems are available from other manufacturers, for example: "Maxima"® (Elgastat), and "Nanopure"®, "E-pure"® or "Easypure"® (Barnstead). The choice of the system and the cartridges selected should be tailored to the suit the specific analytical requirements.

## 8. Purification of inorganic acids for trace metal analysis

### 8.1. Acids other than hydrofluoric acid (HF).

Sub-boiling distillation from a still made of vitreous silica (quartz) of the type depicted in Figure 3 is a highly effective and convenient method for purification of all inorganic acids other than hydrofluoric acid (HF) (see Section 8.2. for the purification of HF). An electric resistance heater evaporates the acid from the liquid surface, and the vapour is condensed on the surface of a cold finger condenser. The condensate is collected in small (100 ml) quartz bottles.

A new apparatus has to be conditioned by repeated distillation of, each time, fresh batches of the acid to be purified, until satisfactory blank values are obtained.



**Figure 3. Quartz apparatus for sub-boiling distillation of acids (excluding HF)**  
(See Section 8.1.)  
1 is the heating element; 2 is the cold finger condenser

(Figure courtesy of Hans Kürmer, Analytentechnik, Herderstrasse 2, D-8200 Rosenheim)

### 8.1.1. Equipment

Quartz sub-boiling distillation apparatus of the type shown in Figure 3.  
Variable transformer or solid state thyristor power controller  
quartz storage bottles  
laminar flow hood

### 8.1.2. Procedure

The distillation apparatus is set up in a laminar flow hood. This is important because distillation in potentially contaminated and dusty ambient air involves a high risk of disappointing results. The feedstock is analytical grade acid. The quartz distillation apparatus is filled, through the filling nozzle, with the acid to be purified, until the proper liquid level is reached. The cooling water is turned on, and the power is adjusted so that one drop of distilled acid is collected about every four seconds. At this rate, approximately 100 ml are collected in eight hours.

### 8.1.3. Cleaning of the quartz still

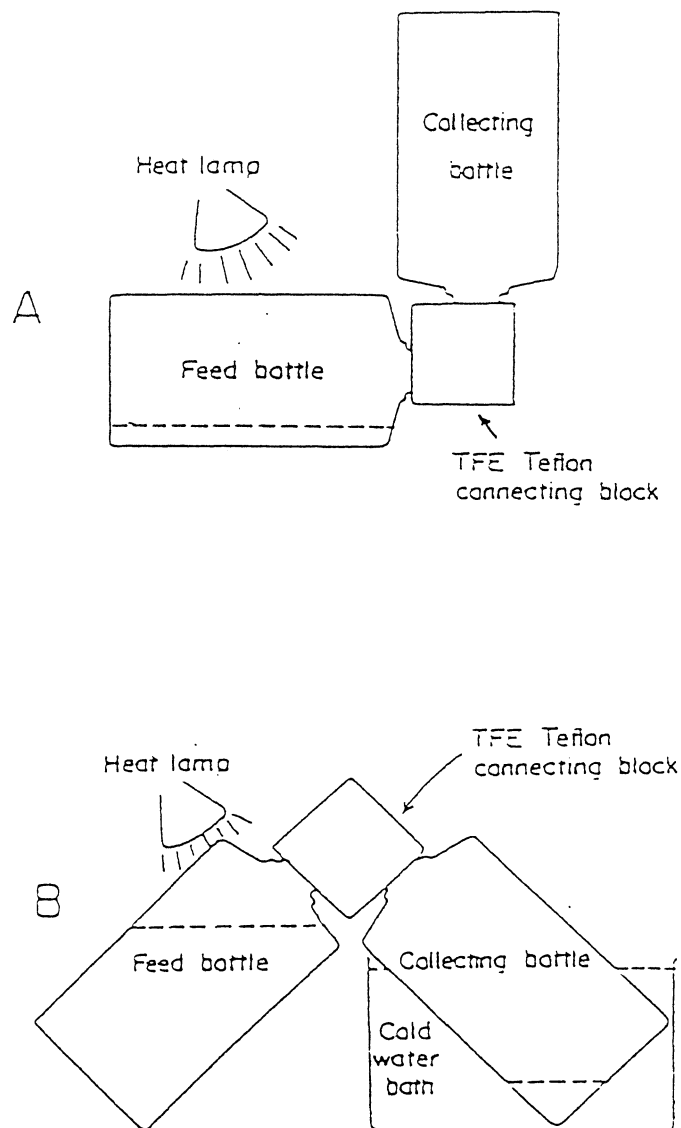
As a routine safety measure, twice a year, and certainly if blanks should become unsatisfactory, the quartz still is thoroughly flushed with ultrapure water (see Section 7). Without drying the interior, acid is poured in and distilled in the manner described above. The initial 10% (the forerunnings) are discarded. This procedure is repeated 2-3 times until adequate blanks are obtained.

## 8.2. Purification of hydrofluoric acid

**Extreme caution!** As its vapours are highly poisonous, hydrofluoric acid must only be handled and distilled under a fume hood. It is absolutely essential to wear gloves. Hydrofluoric acid penetrates the skin causing painful and long lasting sores as well as permanent damage by bone dissolution. Fingertips are particularly sensitive, as adhering acid is hard to remove from underneath fingernails. An especially malicious aspect is that damage usually becomes apparent only the next day and may then be irreversible. Immediate neutralization with aqueous bicarbonate solution is a first emergency measure; a physician must be consulted without delay.

### 8.2.1. Equipment

Because HF reacts with silica to form  $\text{H}_2\text{SiF}_6$  and water, a still for its purification has to be made of an inert material other than quartz. Distillation apparatus of the same basic design as that described in Section 8.1., but made of Teflon, are commercially available. One should be aware, however, that gaskets not entirely resistant against HF may be sources of contamination.



**Figure 4. Sub-boiling distillation apparatus for acids (including HF)**  
(See Section 8.2.)

A is the cleaning position; B is the collecting position

Figure taken from: Mattison, J.M. 1972. Preparation of hydrofluoric, hydrochloric, and nitric acids at ultralow lead levels. *Anal. Chem.*, 44 (9): 1715-1716.

A rather simple yet highly effective sub-boiling still without any gaskets and suitable for all acids has been described by Mattison (1972) (see Figure 4). It consists of two FEP (Fluorinated Ethylene Propylene) Teflon (Nalge Company) bottles of suitable capacity (250-1000 ml) which are connected at right angles by a threaded PTFE (PolyTetraFluoroEthylene) block (Figure 4). Such a block can be made by any competent machine shop with threading tools. An infrared heat source (directed, from above, at the liquid surface in the feed bottle containing the reagent to be purified) evaporates the acid below its boiling point. The acid vapours are condensed in the ice-water cooled collecting bottle.

### 8.2.2. Procedure

During distillation, the collecting bottle should be unscrewed about a quarter turn to allow for pressure equilibration. The distance of the heat source to the feed bottle must be adjusted so that no bubbles form in the acid and evaporation is strictly from the surface. Bursting bubbles inject microscopic droplets into the gas phase which may contaminate the distillate.

Using 1000 ml feed and collecting bottles and operating the still under optimum conditions, i.e. cooling the collecting bottle with ice-water, 150-350 ml of HF or HCl can be distilled per day. Due to its higher boiling point, the yield of HNO<sub>3</sub> is approximately 100 ml per day.

### 8.2.3. Cleaning of the still

A new still must be cleaned thoroughly before use according to the instructions given in Section 4.2. Approximately 100 ml of acid are then added to the feed bottle, the still is assembled, and distillation is started with the collecting bottle in a vertically upright position. This way the collecting bottle acts as a reflux condenser, and impurities remaining after the preliminary cleaning are refluxed into the feed bottle. The still is operated in this position for several days. The acid in the feed bottle is changed 2 or 3 times.

## 9. Sources of reagents and apparatus

The following list provides examples of suppliers of the equipment and reagents referred to in the text. It is not exhaustive and does not suggest an endorsement of quality:

- ◆ Aldrich Chemical Company, 1001 W. Saint Paul Ave., Milwaukee, WI 53233, U.S.A.  
Fax: 1-414-273 4979.
- ◆ Bioblock Scientific, Parc d'innovation, Strasbourg-Ilkirch, B.P. 111-67403 Illkirch Cedex, France. Fax: 33-88 67 11 68. Phone: 33-88 67 14 14.
- ◆ Barnstead (available through Cole-Parmer Instrument Co.).
- ◆ Carl Roth GmbH & Co, Karlsruhe, Germany. Fax: 49-(0)721 56 06 49.
- ◆ Cole-Parmer Instrument Co., 7425 North Oak Park Avenue, Niles, Illinois 60714, U.S.A.  
Fax: 1-708-549 1700. (many local distributors).
- ◆ Elgastat, 13, Rue Bourgey, F-69100 Villeurbanne, France. Fax: 33-78 68 94 58
- ◆ Lab. Safety Supply, International Division, P.O. Box 1368, Janesville, WI 53547-1368, U.S.A. Fax: 1-608-754-7160.
- ◆ Merck, E. Frankfurter Strasse 250, Darmstadt 1, D-6100, Germany. Phone: 49-6151-720.  
(many local distributors).
- ◆ Millipore Corporation, Ashby Road, Bedford, MA 01730, U.S.A. Fax: 1-508-624 8630.  
(many local distributors).
- ◆ Nalgene Company, Subsidiary of Sybron Corporation, 75 Panorama Creek Drive,  
P.O. Box 20365, Rochester, NY 14602-0365, U.S.A. Fax: 1-716-264 3706.  
(many local distributors).
- ◆ Rudolf Brand GmbH & Co., P.B 1155, Wertheim, Germany. Fax: 49-9342-80 82 36.

### Suppliers of distillation apparatus:

#### Glass stills:

- ◆ Erich Eydam KG, P.O. Box 2049, D-24119 Kiel-Kronshagen, Germany.  
Fax: +49 (0)431 5480755; Phone: +49 (0)431 548070.
- ◆ Normschliff Gerätebau, P.O. Box 1554, D-97877 Wertheim, Germany.  
Fax: +49 (0)9342-80928; Phone: +49 (0)9342 8215-8218.

#### Quartz stills and teflon stills:

- ◆ Hans Kürner Analysentechnik, P.O. Box 171, D-83022 Rosenheim, Germany.  
Fax: +49 (0)8031-88088; Phone: +49 (0)8031 17034.

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