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G. Knapp^a

^a Institute for Analytical Chemistry, Micro- and Radiochemistry, Technical University Graz, Graz, Technikerstrasse, Austria

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Sample Preparation Techniques—An Important Part in Trace Element Analysis for Environmental Research and Monitoring†

G. KNAPP

Institute for Analytical Chemistry, Micro- and Radiochemistry, Technical University Graz, A-8010 Graz, Technikerstrasse 4, Austria

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KEY WORDS: Environmental samples, sample preparation techniques, decomposition methods, trace elements, ashing, X-ray fluorescence spectrometry, preconcentration.

For the determination of minute amounts of elements in environmental samples combined analytical procedures are frequently employed. The combination of suitable sample preparation techniques with adequate detection methods lead to powerful analytical procedures. Decomposition methods are an important part of combined procedures for the determination of trace elements in solid samples. After a short summary of the potential sources for systematic errors two new decomposition methods are described that are suitable for the ashing of organic environmental samples. In one method the organic sample is ashed in a high-frequency excited oxygen plasma. The second method is a high pressure decomposition that permits mineralization of the sample in sealed quartz vessels with nitric acid at temperatures up to 320°C.

For both methods the ratio of sample weight to decomposition reagents is comparatively high. This makes these methods in combination with adequate

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detection methods suitable for the determination of elements at very low concentrations.

X-ray fluorescence spectrometry combined with adequate preconcentration methods is very well suited for the simultaneous determination of trace elements. Following a critical evaluation of various preconcentration techniques the analytical characteristics of filter paper with immobilized complexing agents are described. Particular emphasis is given to filter papers with dithiocarbamates as chelating group.

INTRODUCTION

The demand for analytical methods to determine trace elements in environmental samples is continually increasing. The first problem to be tackled was the determination of the total element contents of environmental samples in continually smaller concentrations. The necessary analytical methods at hand are already very efficient, however they are constantly being improved. During the past few years scientists have been discovering that the knowledge of the sample's contents is insufficient in many cases in solving problems concerning the environment because the effect of an element depends to a large extent upon its compound structure. Under the title of "Speciation" the analytical methods for determining the various element species have been developed. This line of research still is in the initial phase. So-called "Direct Methods" for measuring samples directly are the ultimate goals but are as yet only available for few selected cases. Most problems are solved by analytical multistage methods.

For determining the total element contents the decomposition of solid inorganic and biological materials is of significant importance. A method combined of sample decomposition and an efficient measuring system can solve many problems of environmental analysis. Additional preconcentration or separation methods will only be necessary if the sensitivity or the selectivity of the measuring method is insufficient.

For determining element species an efficient separation method combined with a measuring method is necessary. The separation method can only be avoided if the measuring system reacts selectively to element compounds or certain oxidation states of an element. With multistage methods for determining species the main attention of the present analytical research and development focuses

on the following steps of analysis:

- 1) Isolation of the element species from the sample matrix.
- 2) Separation of the various element species.
- 3) Interfacing between separation and measuring system.

In the following, efficient multistage methods for determining the total element contents of environmental samples with the help of newer sample preparation methods will be referred to. Whereas measuring methods are frequently reported, the sample preparation techniques and, in this connection particularly, the decomposition methods are hardly noticed. But the sample preparation as well as the measuring method must be efficient and free of systematic errors in order to achieve a sufficient multistage procedure.

SYSTEMATIC ERRORS IN SAMPLE PREPARATION METHODS

The causes of systematic errors in the various sample preparation steps are dealt in literature.¹⁻⁷

Contamination

The contamination of the sample by the atmosphere is smaller in closed systems than in open systems. The contamination by reagents can be reduced by using a minimum of suprapure reagents. Liquid reagents of good volatility (HNO_3 , HCl , HF , H_2SO_4 , HClO_4 , NH_4OH , H_2O) can be obtained in great purity by sub-boiling distillation.⁸ Figure 1 shows the line drawing of a sub-boiling distill.

Volatilization

The volatilization of elements is a major error source in many decomposition methods. Through the use of closed systems this source can be eliminated in most instances. If open systems are used the losses of elements can be kept within predictable limits if certain experimental parameters are closely controlled.

Adsorption and desorption

The material of the reaction vessel is also a frequent source of

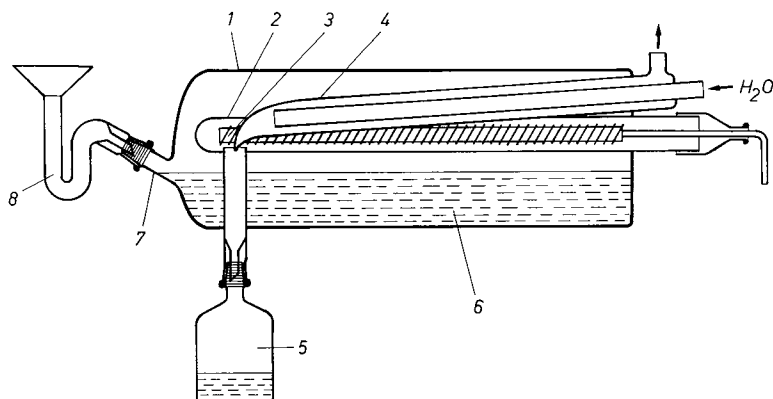


Figure 1 Drawing of a sub-boiling quartz still (1) distillation chamber, (2) quartz tube, (3) heating filament, (4) cooling finger, (5) bottle with purified acid, (6) acid to be distilled, (7) connector, (8) inlet funnel.

systematic errors. Elements can be either dissolved from the material, desorbed from or adsorbed on the vessel surfaces. Very important in this respect is the nature of the material. In general quartz, but also PTFE and glassy carbon have proved to be suitable. At extreme trace levels the steaming of vessels with nitric acid is very advisable. The surface is thus cleansed of adsorbed species and conditioned in a way that reduces significantly adsorption processes.² Figure 2 schematically shows an apparatus for the steaming of vessels.

Sample decomposition

Two recently developed ashing methods totally meet the indicated trace analytical demands and have been applied successfully in environmental analysis.

Cool plasma asher (CPA)†

Figure 3 shows the flow chart of the ashing process. In the well-known manner the organic sample is decomposed at low temperature by a high frequency induced oxygen plasma. As opposed to

†Source of supply: Hans Kürner, D-8200 Rosenheim, Herderstr.2, FRG.

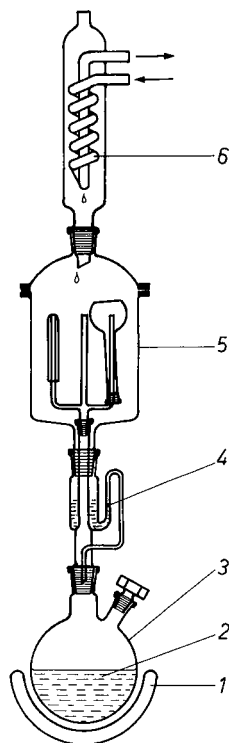


Figure 2 Drawing of a steaming apparatus. (1) heater, (2) nitric acid, (3) round flask, (4) siphon, (5) steam chamber, (6) reflux condenser.

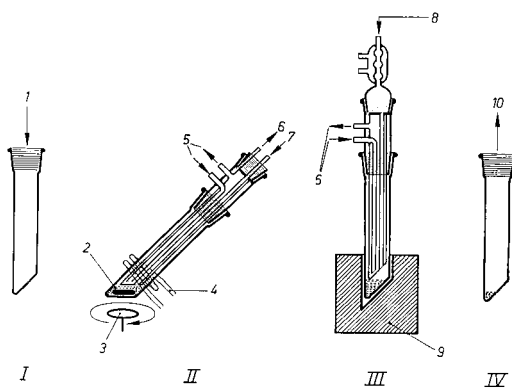


Figure 3 Cool Plasma Asher flow diagram of the ashing process. (I) sampling, (II) ashing, (III) refluxing, (IV) measurement. (1) sample, (2) stirring bar, (3) magnetic stirrer, (4) HF coil, (5) cooling water, (6) vacuum, (7) oxygen inlet, (8) acid, (9) heating block, (10) measurement of the solution.

other commercial versions of the plasma asher, in the CPA the sample is contained in a quartz test tube that is equipped with a cooling finger.⁹ Volatile elements such as arsenic, selenium and others that are partially lost in traditional plasma ashers are retained on the cooling finger during the ashing process. Mercury however is lost. After the destruction the liberated elements are dissolved by refluxing in 1–2 ml acid.

An advantage of this method is that the elements are present afterwards in comparatively high concentration. Up to 1 g sample material can be ashed and the liberated elements can be collected in just 2 ml ultra pure acid by refluxing. For environmental analysis this method is perfectly suitable for destroying dust collecting filters made of cellulose or polymers. Even PTFE can be ashed by this method. The inorganic part of the collected dust remains in the quartz test tube for further processing.

High Pressure Asher (HPA)†

One of the most prominent decomposition methods during the past years has been the wetchemical decomposition with nitric acid in PTFE bombs. Bomb decompositions offer the great advantage that many substances which are inert towards nitric acid at lower temperatures may be attacked successfully at higher temperatures, and also an additional bonus is that the loss of volatile reaction products is avoided, unless of course there is an escape of gases when the bomb is opened after cooling. This method however is hampered by grave disadvantages. The decomposition temperature must not significantly exceed 200°C. Frequently, the decomposition process at this temperature proceeds sluggishly and will be incomplete. PTFE absorbs, in certain cases, elements from the solution or, alternatively, leaks them to the solution. Losses or contamination are the consequences.

To avoid these problems we use vessels of pure quartz (Figure 4) in our new pressure decomposition.¹⁰ These quartz vessels are covered by a quartz lid with a ground bottom surface. This vessel is then mounted in an autoclave (Figure 5) provided with a heated aluminium-block and subjected to a pressure of 100 bar. A gas

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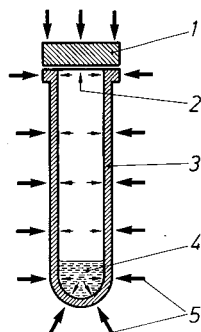


Figure 4 High Pressure Asher principle of operation. (1) quartz lid, (2) pressure inside of the decomposition vessel (<100 bar), (3) quartz vessel, (4) sample and nitric acid, (5) pressure outside of the decomposition vessel (100 bar).

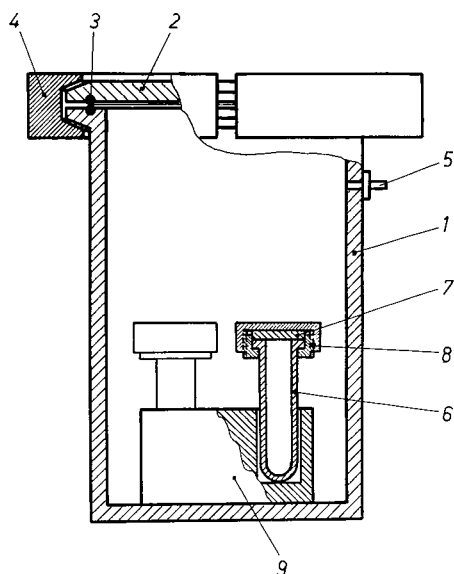


Figure 5 High Pressure Asher autoclave drawing. (1) pressure chamber, (2) lid of the pressure chamber, (3) O-ring, (4) ring retainer, (5) pressure gas inlet, (6) quartz vessel, (7) quartz lid, (8) steel screw cap, (9) heating block.

regulator unit permits a simple filling and emptying of the autoclave, e.g. from a nitrogen tank.

The lid is pressed firmly against the vessel and the vessel is tightly sealed by the ground lips connecting vessel and lid. The vessel is now heated according to a preselected temperature program. The maximum temperature is 320°C. Since the pressure within the vessel is lower than the pressure applied, the vessel is sealed during the decomposition. After the decomposition is complete the pressure in the autoclave is released and the vessel may be opened.

Different sizes of vessels (2–70 ml) are available to optimally decompose samples varying in weight from a few mg to 1.2 g. Depending upon the size of the digestion vessels up to seven units are placed inside the autoclave. The smallest decomposition vessel is built in such a way that it fits into the sample tray of the Perkin–Elmer graphite furnace autosampler (Figure 6). 10–20 mg of sample material are decomposed with 200–500 μl of nitric acid or nitric acid-perchloric acid. For certain elements a suitable matrix modifier is added directly to the decomposition reagent to improve the measurements in the graphite furnace. This process fulfills an important trace analytical principle—using one and the same vessel from sampling to the measurements.

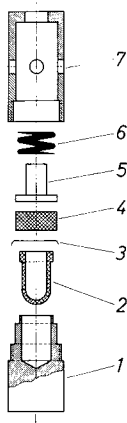


Figure 6 High Pressure Asher drawing of the micro ashing vessel. (1) stainless steel support, (2) quartz vessel, (3) PTFE foil, (4) quartz lid, (5) stainless steel insert, (6) spring, (7) stainless steel screw cap.

A microprocessor-temperature control allows a wide variety of temperature programs. Five different temperature levels and temperature ramps can be preprogrammed. The adaptation of the temperature program to the specific decomposition task is very important. A screen is used to show the programmed and the actual values as well as the pressure inside the autoclave. Using a special cover the pressure inside the digestion vessel is measured and temperature pressure-crucives of decomposition reactions are displayed on the screen.

Many different organic materials such as biological samples, polymers, coal, oil, fat and other organic industrial products can be decomposed by this method, as well.

The combination of decomposition and measuring methods lead to powerful analytical procedures. If suitable separation and preconcentration methods are added, completely novel possibilities for elemental trace analysis open up. I would like to elaborate that point on the basis of an example from our own research. X-ray fluorescence spectrometry coupled to suitable preconcentration procedures permits a rapid multielement analysis in the ng/g and ng/ml range. Particularly suitable for this purpose are preconcentration methods that collect the elements in as thin a substrate of a light element as possible. Ideal carriers are thin membrane filters. For this reason coprecipitation techniques with organic reagents give the best results. In comparative studies the reagent dibenzylthiocarbamate developed by Schreiber¹¹ gave the best results. Depending on the element and the X-ray spectrometer the detection limits of this method are between 50 and 200 ng. How can the preconcentration step be further enhanced?

The amount of work necessary for preconcentration can be minimized if the complexing agents is coupled onto the filter. Conventional cation exchangers suffer from the lack of selectivity with respect to transition elements. Even the Chelex-100 exchanger shows cross-sensitivities from alkali and alkali earth elements. Complexing filter material for the simultaneous preconcentration of trace ions in connection with X-ray fluorescence should have the following properties:

- 1) High useful capacity (expressed in mmol per g filter material).
- 2) Good exchange kinetics of the analytes (permitting a high filtration speed for preconcentration).

- 3) Low area weight (expressed as mg per cm² leading to a good sensitivity in X-ray fluorescence spectrometry).
- 4) Sufficient mechanical stability.
- 5) Low content of heavy metals (low blanks)
- 6) Low affinity towards alkali and alkali earth ions.
- 7) Good long term stability of immobilized chelating groups.

These requirements are partly contradictory and it is difficult to find the optimal compromise. This is a suspected reason why no commercial products are on the market as yet. If trace element ions are to be collected over as wide a concentration range as possible, the useful capacity is of decisive importance. For too low a capacity just those elements are preconcentrated quantitatively that have under the experimental conditions chosen the highest affinity towards the chelating groups. The exchange kinetics of a complexing exchanger is in aqueous solutions largely dependent on the hydrophilicity of the supporting material. For this reason cellulose is a very suitable substrate. The kinetics of chelation is not just determined by the nature of the immobilized chelate but also by the steric environment where complexation takes place. Accordingly, it is important that chelating groups are not immediately affixed to the cellulose fiber, but connected to it by a spacer. Observing these parameters we have synthesized cellulose filter paper with dithiocarbamate, 8-hydroxyquinoline and an EDTA-analogue (Figure 7).¹²

The actual preconcentration step is reduced to a simple filtration step of a pH-controlled solution. The flow rate should be 6–7 ml min⁻¹.

The pH dependence (Figure 8) of divalent ions is fairly typical for dithiocarbamates and recovery is close to complete at pH 5.5. 300 ml volume are used in this case. For ions with more than one stable oxidation state a certain discrimination is possible as shown in Figure 9. For Cr VI, As III and Se IV the recovery can be made quantitative. As(V) is not shown on the slide but also gives low recovery.

As the method is used for preconcentration a look at the detection limits obtained by X-ray fluorescence is advised.

Table I juxtaposes the measured and theoretical detection limits. It can be seen that one comes fairly close to the theoretical limits imposed by Poisson statistics.

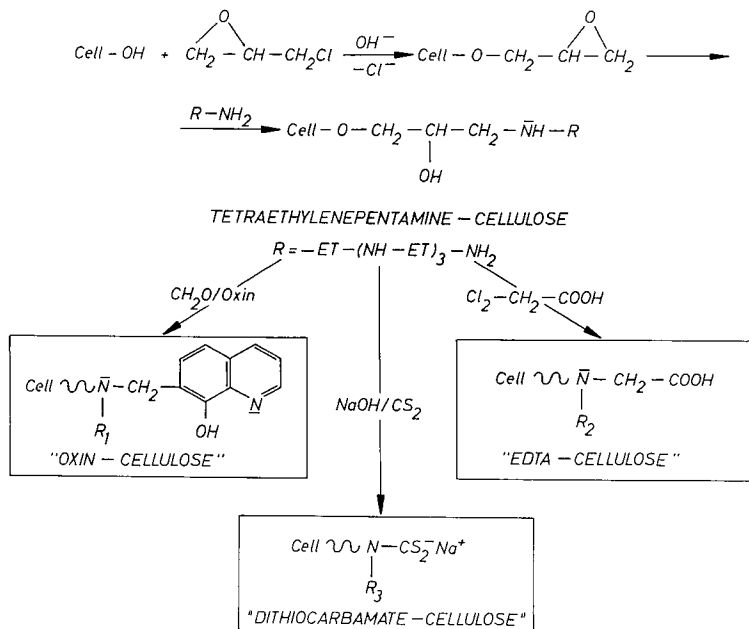


Figure 7 Summary of the synthetic pathways chosen for the production of three different chelating cellulose filters.

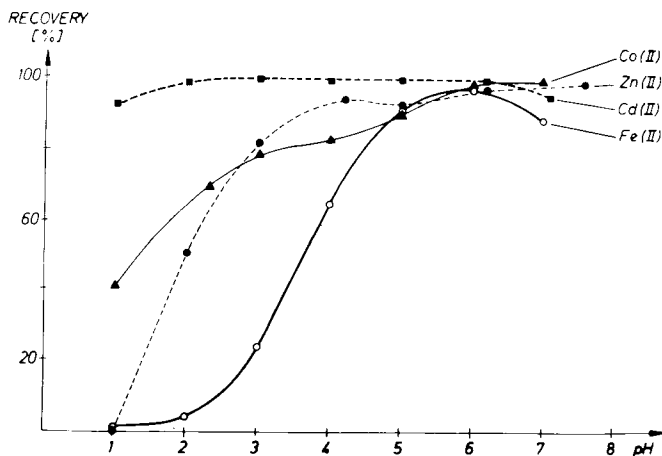


Figure 8 The pH-dependence of divalent ions.

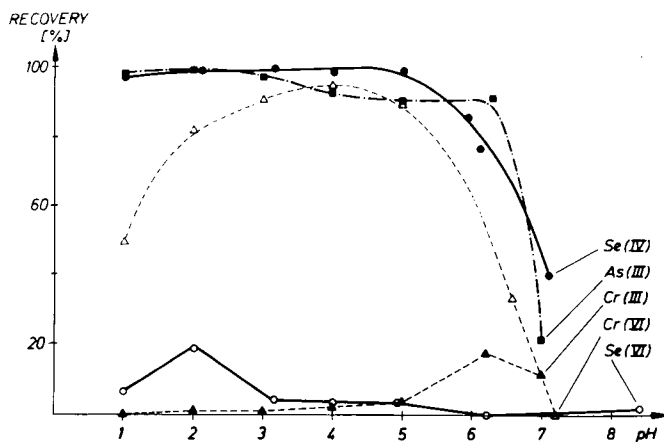


Figure 9 The pH-dependence of polyvalent ions.

TABLE I
Detection limits [$\mu\text{g}/\text{cm}^2$]

Element	Measured	Theoretical
V	0.1	0.087
Mn	0.1	0.1
Co	0.06	0.043
Cu	0.1	0.040
Se	0.06	0.037
Pb	0.1	0.050
Ni	0.1	0.037
Zn	0.15	0.037
As	0.07	0.02
Cd	0.3 (0.15) ^a	0.1

^aNormalized to background.

CONCLUSIONS

In environmental analysis the surveillance of bodies of water very often is difficult because systematic errors due to sampling, transporting and storing of water can not be excluded. By using chelating

filter papers, methods can be developed for concentrating the heavy metal traces at the sampling site.

All this could contribute significantly to a simple and proper surveillance of heavy metals in bodies of water.

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