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MODERN STRATEGIES IN THE DETERMINATION OF VERY LOW CONCENTRATIONS OF ELEMENTS IN INORGANIC AND ORGANIC MATERIALS

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Abstract - Today the analytical determination of very low levels of elements in the ng/g range in high purity metals, solid state materials or biological samples has become more and more a routine task of many laboratories. Although a number of direct instrumental determination procedures with sufficient detection ability are described in the literature, considerable discrepancies have been found for results of real samples. Also the accuracy very often is insufficient.
To overcome these problems a pathway towards high detection ability and satisfactory accuracy leads via multi-stage procedures which can easily by calibrated by aqueous standard solutions. Unfortunately these multi-stage procedures are associated with a number of systematic errors which can not always be easily recognized and reduced.
Main sources of systematic errors are blanks, adsorption and volatilization effects. The actual detection limits of solution procedures are mainly determined by the blanks which occur even in very simple operations e.g. preparation, measuring, storage, filtering or evaporation of solutions.

Possibilities for eliminating these errors are the choice of suitable vessel materials such as quartz, polytetrafluorethylene, polypropylene or glassy carbon and their effective cleaning by a steaming procedure with acid or water vapour and by preequilibration. Blanks from the dust of the air can substantially be eliminated by working in clean rooms and clean benches. Extreme purification of reagents is limited to some liquids such as the acids, water, etc. and done by sub-boiling distillation.
A further contamination of the sample solution cannot be avoided. This is shown by the results of some very simple experiments.
From these facts the methodical strategy for the development of accurate determination procedures in the field of extreme trace analysis is derived and will be demonstrated in general and by means of some case studies.

INTRODUCTION

Today in material science, solid state physics, life sciences, pollution control and many other fields of modern human technology there is a rapidly increasing interest in analytical data in the ng/g and pg/g range both in the bulk of the sample and on the surface as well as of the distribution of the trace elements in micro ranges.

In analytical chemistry many different instrumental multi-element determination procedures are at our disposal and the detection limits reported in the literature are excellent. But even in the bulk analysis in the ng/g range the analytical chemist very often is faced with serious problems showing the limitations of these methods.

The analytical chemistry having an image of very high accuracy and trustworthiness derived from the determination of major components, now seems to be no longer reliable in the extreme range. This is proved again and again by round robin tests (Ref. 1). Although the reproducibility of the results of these interlaboratory comparisons are very good the analytical data in

the field of extreme trace analysis often are incorrect by several orders of magnitude.

Direct instrumental multi-element procedures, e.g. optical emission spectroscopy (OES), X-ray fluorescence spectrometry (XRFS), instrumental neutron activation analysis (INAA) or solid state mass spectrometry (SSMS) at first sight seem to be also the optimal methods for extreme trace analysis, because they require only little sample preparation, thus avoiding contamination and other interferences by the chemical treatment of the sample.

But the instrumental procedures are insufficiently sensitive and suffer from the lack of suitable reference materials which are necessary for calibration and to overcome the very complex interferences inherent in the excitation of the analysis signals.

So we have to give priority to the so called "multi-stage combined procedures", consisting of decomposition, separation, preconcentration and determination steps, which are easy to calibrate by aqueous standard solutions.

Unfortunately these sophisticated and longwinded procedures are subject to a number of systematic errors, which are for the most part due to contamination of the solution causing blanks, and due to losses of the elements to be determined by adsorption and volatilization effects (Ref. 2-7).

The avoidance of these systematic errors requires a great effort (Ref. 3).

The most important sources of systematic errors are:
1) incorrect sampling and sample storage;
2) contamination by vessels, reagents and the dust of the air;
3) adsorption and desorption effects at the surface of the vessels;
4) volatilization of elements like mercury, arsenic , selenium, cadmium and others and compounds like oxides, halogenides, hydrides;
5) matrix effects during excitation of the analytical signals;
6) signal interferences by the background and signals of other compounds;
7) errors in calibration by wrong standards, unstable standard solutions and blanks.

All these systematic errors are by no means easy to recognize and to reduce. As standard reference materials are not available, we have to run interlaboratory comparisons, in which as many laboratories as possible should collaborate. At minimum, two or three different, independent procedures, with different techniques for decomposition, separation and determination must be used.

There are some other means giving some indications like radiotracers, using absolute procedures which need not be calibrated for curious dependences of the analytical results on test portion, day of the week or hour of the day.

Although it is true that reproducible results are by no means a guarantee for accurate results, a bad reproducibility often indicates a systematic error.

SYSTEMATIC ERRORS

It is impossible to give here a comprehensive report on systematic errors, so I have to confine myself to point out only recent results of our investigations in this field (Ref. 8).

Losses of elements due to adsorption

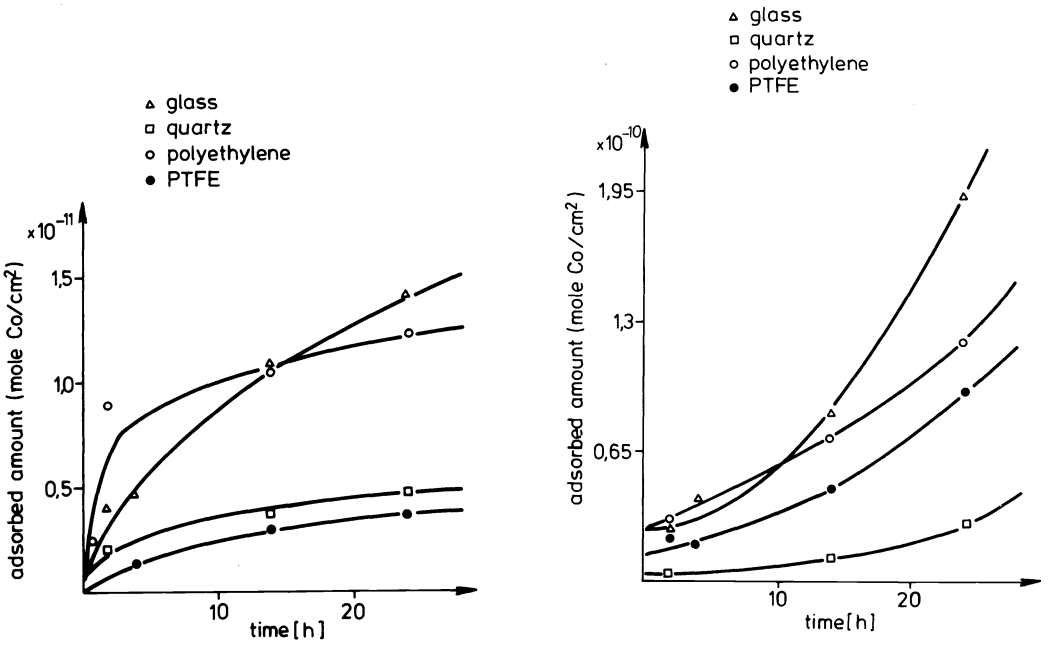
Losses of elements due to adsorption on the surface of the vessels as a rule becomes noticeable at concentrations lower than 10^{-6} molar. The lower the concentration of the element the higher is the loss, which can very easily be monitored by radioactive isotopes.

The amount of the adsorbed element depends upon numerous factors which all have to be specified, if a forecast of the adsorption behaviour of an element is required (Ref. 8&9).

The factors to be taken into account are:
1st) the element itself, its valency state and its concentration;
2nd) the composition of the solution, the pH-value, kind, valency and concentration of other elements, salts, organic components and so on;
3rd) the vessel and its material, composition and purity of the material, dimension and constitution of the surface, pretreatment and cleaning procedures;
4th) time and temperature.

Figures 1a and b give a short impression of the adsorption of cobalt ions on different vessel materials such as glass, quartz, polyethylene and polytetra-

flourethylene (Ref. 8). The concentration of the cobalt(II) in both cases is 2×10^{-5}M (1,2 µg/ml). The only difference causing the big change of the shapes and the order of the curves is the pH value, being in Fig. 1a 1.5 and in Fig. 1b 9.



a) b)

Fig. 1. Adsorption of $^{60}Co(II)$-ions ($2 \cdot 10^{-5}$M).
a) pH = 1.5; b) pH = 9.

As a rule, glass is adsorbing a much larger part of the trace element content than quartz, PTFE or glassy carbon do. Most important is a very good cleaning of the vessel surface. A treatment of the vessel with steam of nitric or hydrochloric acid or water for several hours will lower to a great deal elemental losses.

Blanks from the vessel and the vessel material

As no vessel material is realy totally resistant even to water, each element of the vessel material will be found at a more or less high level in a solution in the vessel. As glass is a very impure material with a few main components and a large number of elements in the µg/g range, this will not be suitable for extreme trace analysis. So we have to prefer quartz, glassy carbon or PTFE (Ref. 8).

Quartz is available in different purity classes. It is definitely the purest material and acid solutions stored in it acquire only few impurities. PTFE and glassy carbon are substantially less pure. However, glassy carbon delivers only few impurities after a steaming pre-treatment because diffusion in the bulk is avoided by its structure. PTFE, however, is permeable for many substances, e.g. gases.

Besides the purity of the vessel material, also the cleaning procedure for the vessel is of very great importance. Scouring powders, soaps and detergents or chromic-sulfuric acid as well as automatic dishwashers are not suitable as they will contaminate the glassware more than they will clean them. The most usual way of cleaning laboratory glassware is rinsing it with acids and pure water. To find out the best procedure we used special 2 ml-beakers made of glass (Duran D50), quartz, PTFE and glassy carbon (Fig. 2) with a cover out of PTFE. To avoid contamination by handling, they were touched only by PTFE covered crucible tweezer underneath the pad, shown in Fig. 2. These small beakers were not used before to have full control of the pretreatment.

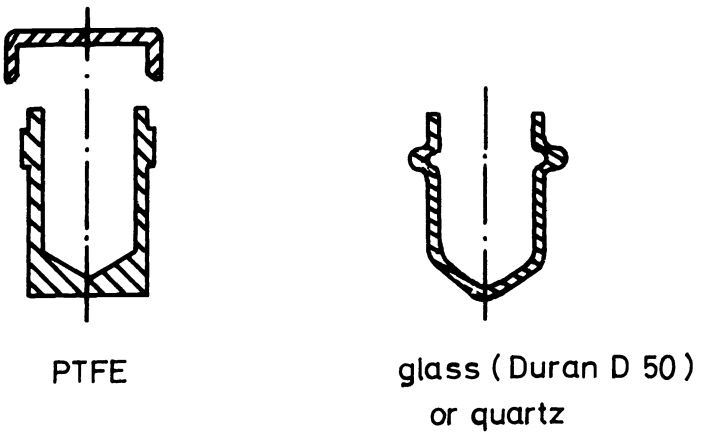


Fig. 2. 2 ml vessels.

Zinc and Magnesium being two elements with serious blank problems in extreme trace analysis were chosen as test elements. Atomic absorption spectrometry with electrothermal atomization (ETA-AAS) was used as determination procedure having a limit of detection for both elements in pure water solution of 0.02 ng/ml. Nitric and hydrochloric acids, purified by sub-boiling distillation as well as bidistilled water had a zinc- and magnesium content equal or below the limit of detection. All experiments were carried out in a clean room.

After cleaning the vessels by steaming they were contaminated by a solution containing 0.1 µg/ml of zinc or magnesium for about two hours and then rinsed by filling it with double distilled water which immediately was poured out. After that the beaker was again filled with water, the zinc and magnesium content of which was measured after a few minutes of standing time.

Figure 3 shows the magnesium content of these water samples. The contamination depends on the pretreatment and on the vessel material.

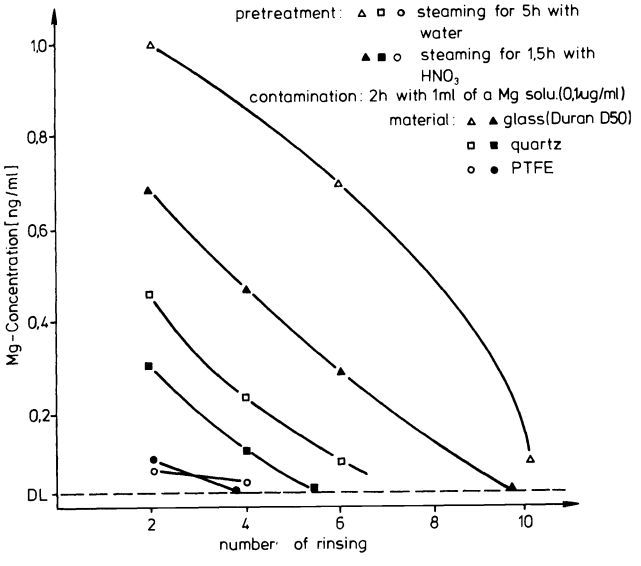


Fig. 3. Magnesium content of water in 2 ml vessels after rinsing.

Here PTFE is best, giving only negligible blanks. Quartz vessels were clean after six times of rinsing, the glass beakers need more than ten times of rinsing.

Much worse was cleaning of volumetric flasks which were contaminated by magnesium-solutions with concentrations of 0.1, 2 and 10 µg/ml. Figure 4 demonstrates that there is no possibility of cleaning flasks by rinsing. Even after seven times of rinsing with hydrochloric acid and 18 times of rinsing with water, the water sample filled in afterwards showed eminently high

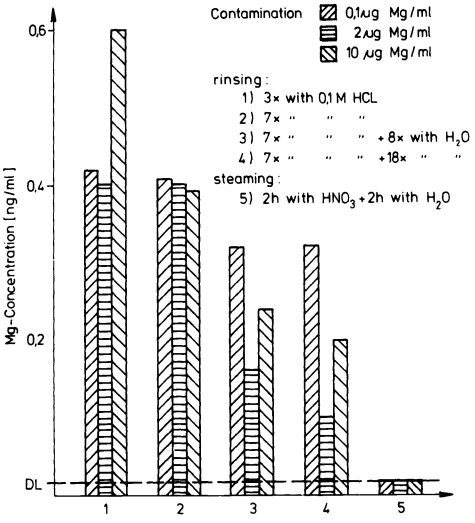


Fig. 4. Magnesium content of water in 50 ml flasks after different cleaning procedures.

blanks. Only in experiment no. 5 results were equal or below the detection limit.

Cleaning by a treatment with acid or water vapour

Figure 5 shows an apparatus with which the very low blanks of experiment 5 were obtained (Ref. 8). Acids such as nitric or hydrochloric acid are heated

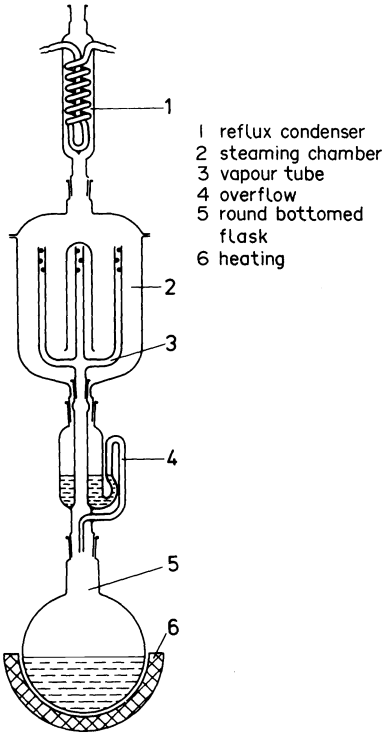


Fig. 5. Steaming apparatus for vessel purification in nitric acid vapour or water vapour.

to boiling in a roundbottomed flask. The vapours pass a tubing system and wash mainly the inner surface of the test tubes, flasks and bottles hanging on top of the tubes inside the steam chamber. Only these tubes coming in contact with the laboratory glassware are made of quartz whilst the other parts of this apparatus are of glass.

The vessels are steamed with the acid steam up to six hours (Fig. 6), after-

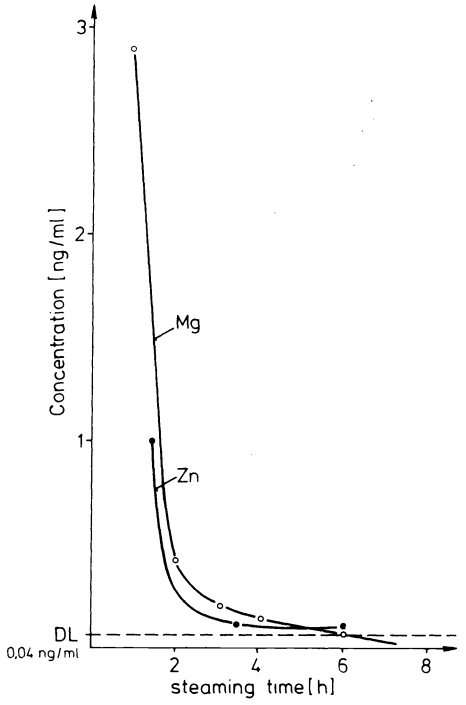


Fig. 6. Magnesium and zinc content of water in quartz vessels depending on the steaming time.

wards they will be treated for another two hours with water vapour. It is only after this procedure that we may have absolute certainty, that the vessels are clean enough for extreme trace analysis purpose. Also losses by adsorption are reduced.

Blanks from the reagents

As there is also no reagent being absolutely pure, we also have to take care to lower the blanks of these substances. Unfortunately the possibilities of purifying the reagents are very limited. Solid substances normally require laborious and sophisticated procedures similar to analytical techniques used for separating elements from the matrix. In most cases we only succeed in decreasing the blank concentration for one or only a few elements whereas that of others might be increased. So in extreme elemental trace analysis we have to avoid solid reagents and use only such ones which can easily be purified, such as gases and most of the laboratory acids.

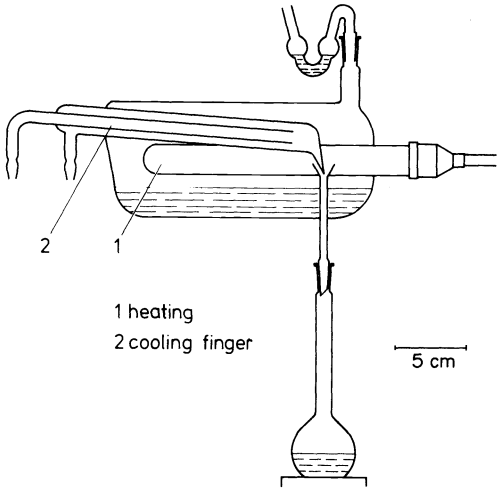


Fig. 7. Sub-boiling distillation still (after Kuehner et al. (Ref. 10)).

Especially the sub-boiling distillation after Kuehner et al. (Fig. 7) (Ref. 10) is a very effective purification technique for hydrochloric, nitric, perchloric and hydrofluoric acid. The obtained blanks for most elements are in the range below 1 ng/ml (Table 1).

The acids are heated up in a quartz still - for hydrofluoric acid it is made of polypropylene - containing a few hundred milliliters, by a pair of quartz covered infrared radiators which are not allowed to dip into the liquid. By the radiation, the acid is not allowed to boil; it only evaporates.

The condensing cold finger is tilted downward to allow the condensed liquid to drop through a funnel into the quartz receiver. Since it is not convenient to produce more than the daily required amount of acid due to unavoidable contamination the output of distilled acid of this small still in the range of some 100 ml per day is more than sufficient.

TABLE 1. Residual impurities in different acids [ng/ml]

		Cd	Cu	Fe	Al	Pb	Mg	Zn
H_2O	sub.b.	0,01	0,04	0,32	≤0,05	0,02	≤0,02	≤0,04
HCl 10M	sub.b.	0,01	0,07	0,6	0,07	<0,05	0,2	0,2
HCl 12M	z.A.	0,1	1	100	10	0,5	14	8
HCl 10M	suprap.	0,03	0,2	11	0,8	0,13	0,5	0,3
HNO_3 15M	sub.b.	0,001	0,25	0,2	≤0,005	≤0,002	0,15	0,04
HNO_3 15M	z.A.	0,1	2	25	10	0,5	22	3
HNO_3 15M	suprap.	0,06	3	14	18	0,7	1,5	5
HF 54 %	sub.b.	0,01	0,5	1,2	2	0,5	1,5	1
HF 48 %	z.A.	0,06	2	100	5	4	3	5
HF 40 %	suprap.	0,01	0,1	3	1	3	2	1,3

Blanks from the dust of the air

Dust particles from the air, which contain a lot of contaminating elements like Si, Ca, Al, Mg, Fe, Na, K, P, as major components and, additionally, nearly all other elements up to an interfering level, may sometimes be excluded by relatively simple means. In special cases, it is possible to arrange a closed system, in which all steps of a procedure can optimally be manipulated. Sometimes glove boxes may be helpful, but to work in them is very inconvenient. In all other cases, clean benches and clean rooms are to be preferred (Fig. 8) (Ref. 1,6,8&11).

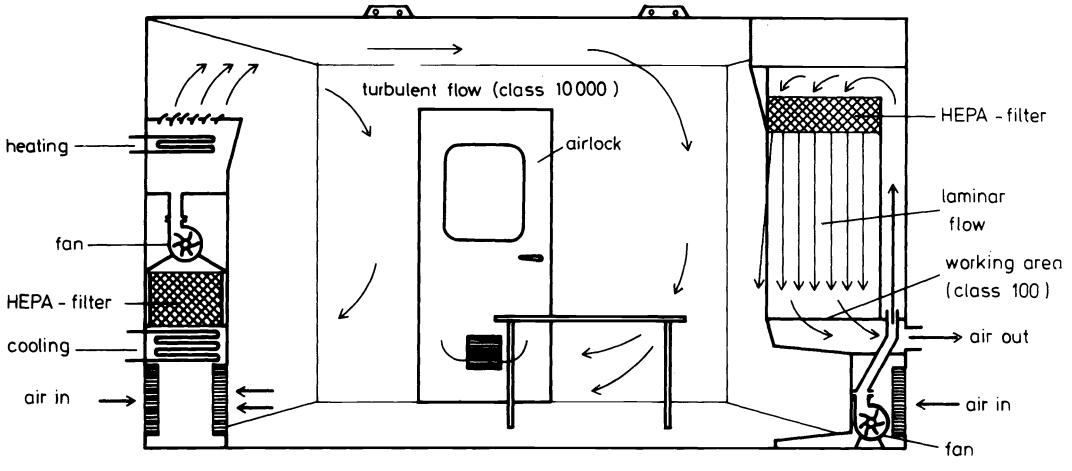


Fig. 8. Cross section of a clean room with a clean bench.

The closed room can be entered only through an air lock. A filter assembly provides pure air, and ensures a circulation in this example with turbulent flow.

The important part of the assembly is the so called HEPA-filter (high effi-

ciency particulates air filter), having a definite pore size of o.3 µm. The degree of deposition lies at 99.97 - 99.995 %.

Side by side with the filtering of the air, the machine cools, heats and regulates the humidity of the air. On the right side of Fig. 8 a cut away view of a clean bench, the actual working place, is to be seen. A ventilator takes in air from outside or from the clean rooms and leads it through another HEPA filter. The air flows from above in a laminar displacement stream through the working room and over the bench. The dust level of the air in the clean bench by the laminar flow is by about 1 order of magnitude lower than in the room where turbulent air takes up dust from steadily present air turbulences.

The degree of purity of the air which can be attained depends on:
1) the filter to be used;
2) the air flow in the room;
3) the air flow pattern;
4) the quantity of the air flow and the velocity of the air;
5) the impurities emitted by tools on the clean bench;
6) the work itself ;
7) the people working in the room;
8) interactions with adjacent benches.

The dust content of the air is classified in terms of standards of cleanliness. Thus, there exists, for instance, in the USA the Federal Standard 209 which specifies the content, per cubic foot, of particles with a diameter between 0.5 and 5 µm (the classes are 100, 10 000 and 100 000).

Figure 9 shows the dust content of a clean room and a normal laboratory, in

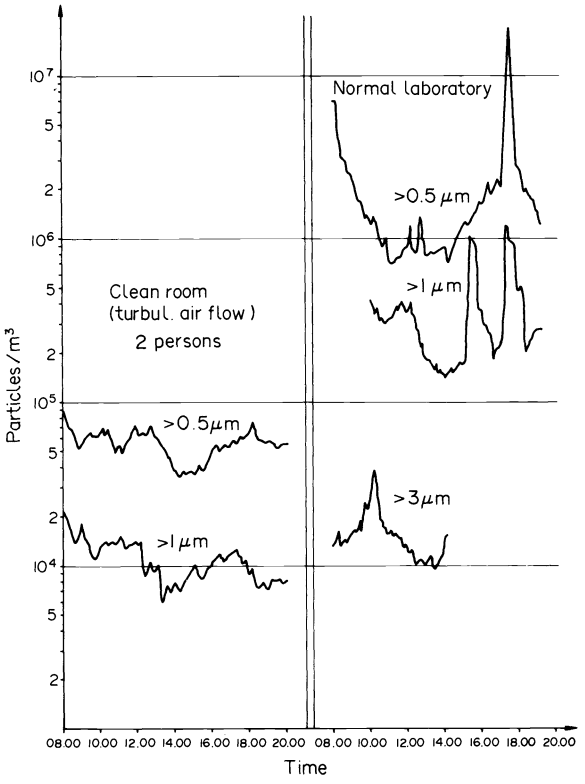


Fig. 9. Dust content of the air of a clean room and a normal laboratory during a day.

the course of a day. At first sight the scattering of the values in the normal laboratory are striking, as well as the relatively strong decrease of the particle content at noon which, on one side, shows the severe load of the room by the operators (2 persons), and on the other side demonstrates the speed with which such an installation purifies itself.

The aforementioned outline of a clean room illustrates only one of the many possibilities of a set up. In this, there is a difference by one class of cleanliness between bench and room. When it is aspired to keep the whole room as dust free as possible, it can only be achieved by a laminar air flow. Then either a wall or the ceiling of the room has to be laid out with filters. Numerous rules have to be taken note of for an effective working in clean

benches and clean rooms as regards the arrangement of the bench, an ingenious procedural system and a highly pure working style.

It is obvious that a high degree of cleanliness has to be adhered to. This applies both for the bench, for devices, and for the operator himself who spreads most of the uncleanliness in the clean room. Also the laminar air flow must not be interfered with by tools or labouring at those places which are to be protected from dust. These places, e.g. all openings of vessels and devices of analysis have always to be scavenged with pure air.

Contamination by analytical working

As metioned before, in spite of the very effective cleaning and purification techniques such as steaming, sub-boiling distillation and of the working in clean benches, one cannot avoid further contamination during the analytical procedure (Ref. 8). Already very simple working steps can seriously increase the blanks. As an example the results of a very simple experiment are presented here. The 2 ml vessels of Fig. 2 are filled with pure water having a zinc and magnesium content equal to or $<$ the detection limit of 0,02 ng/ml. It makes a big difference whether the vessels are emptied by simple shedding or by taking off the solution with a pipette. If the solution was spilled over the brim of the vessel, not only the spilled water was contaminated but also the now empty vessel. If it was filled again with a new portion of pure water the content of magnesium rose to about 3 ng/ml and that of zinc to 0.1 ng/ml. The factor was higher than one order of magnitude. If there was a joint stopper at the vessel, the increase in the blanks was much higher. But by taking off the solution by a pipette, no contamination appeared.

Figure 10 shows the results of a similar experiment where calibrated quartz flask (100 ml) with a joint stopper were used. The flasks were cleaned by steaming with nitric acid for 4 hours and with water for 2 hours, then they were filled with pure water. 2 ml-samples were taken by different techniques

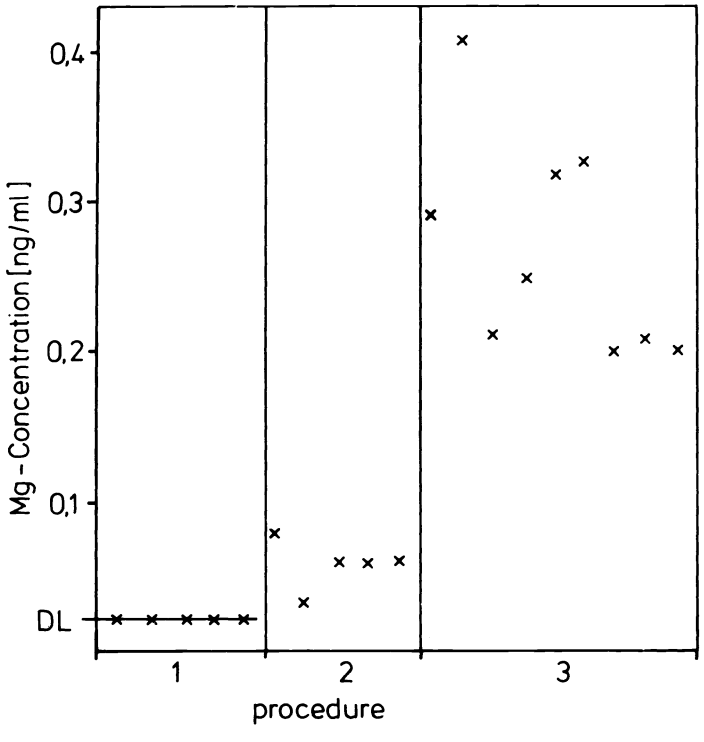


Fig. 10. Contamination of water by magnesium in 100 ml quartz flask.

and the Mg content of the samples were measured by ETA-AAS. If the sample was taken by a quartz pipette without shaking of the flask, no contamination was found. If the flask was shaken before pipetting, the blank value for magnesium was a little bit higher than the detection limit. However, if the sample was taken after shaking by pouring the water out, not only the magnesium content was up to 0.4 ng/ml but also the results of the measurement scattered over a large range.

During storage of pure solutions normally the blank content increases with time. This contamination depends very strongly upon the pretreatment and the cleaning procedure of the vessel (Ref. 8). This is shown in Fig. 11. It is

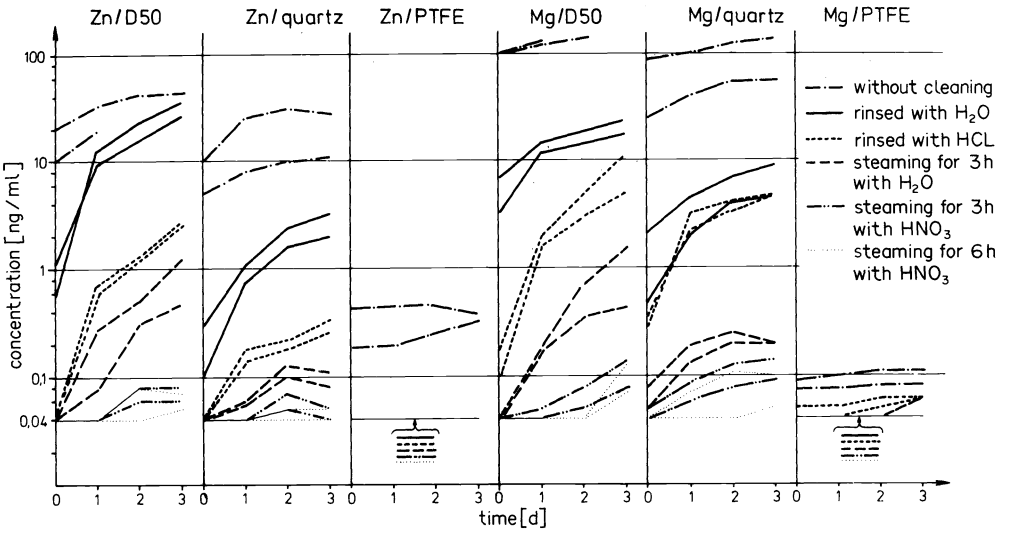


Fig. 11. Contamination of water during storage in 2 ml vessels.

only in vessels steamed for 6 hours with nitric acid that increase in the blanks for magnesium and zinc over a storage period up to three days is negligible. After cleaning only by rinsing, the blanks increased by upto a factor of 100. Best results were obtained with PTFE vessels.

It is obvious that operations not so simple, like shedding and pipetting cause higher contaminations. For instance, filtration or evaporation of solutions enhances the zinc and magnesium content upto more than two orders of magnitude depending strongly upon the conditions. Thus pure water filtered or evaporated in a clean bench do not pick up more than 10 to 50 pg magnesium or zinc per ml, whilst the blanks in a one molar hydrochloric acid evaporated in a normal laboratory will be increased considerably.

What is so alarming with these results is not the true value of the detected contamination, but the fact that the controlled operations are so simple and that these systematic errors will be added during the analytical procedure to amounts lying in the ng/ml range - a range in which numerous analyses were done every day. This means also that for working below the ng/g range a number of conditions have to be fulfilled.

BASIC RULES FOR EXTREME TRACE ANALYSIS

Having in mind all facts of systematic errors, we now are able to summarize the basic rules for extreme trace analysis which have to be obeyed if we want to have a chance to get results in the ng/g and pg/g range with a high degree of precision and accuracy (Ref. 2).

1) All materials used for apparatus and tools must be as pure and inert as possible. These requirements are only approximately met by quartz, PTFE, glassy carbon and to a lesser degree by polypropylene.
2) Cleaning of the apparatus and vessels by steaming is very important to lower blanks as well as element losses by adsorption.
3) To minimize systematic errors, we should prefer microchemical techniques with small apparatus and vessels with an optimal ratio of surface to volume. All steps of the analytical procedure such as decomposition, combustion, separation, preconcentration and determination should best be done in one vessel. If volatile elements or compounds have to be determined, the system should also be closed off against outside and the temperature should be as low as possible.
4) Reagents, carrier gases and auxiliary materials have to be as pure as possible. Reagents which can be purified by sub-boiling distillation are to be preferred.
5) Contamination from laboratory air has to be excluded optimally, by clean benches and clean rooms. By this the blanks caused by the dust can be decreased by at least 2 - 3 orders of magnitude.
6) Low and constant reaction temperature.
7) Manipulations and different working steps are to be restricted to a minimum

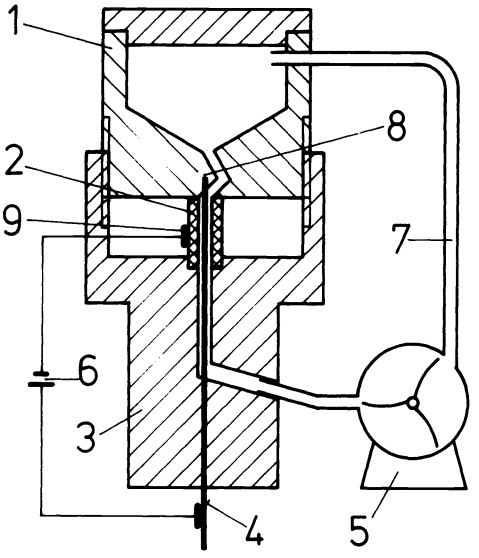
in order to minimize unavoidable contamination.
8) As we can by no means absolutely assure that our analytical results are accurate, we have to control all steps of the combined procedure. This can be done best with radio tracers.
9) All procedures have to be controlled by a second independant one, or even much better by an interlaboratory comparison.

We also have to answer the question of which is the best procedure for a well defined analytical problem, as there is no universal and absolute "best" procedure. For both, the instrumental and the combined procedures, important criteria for the choice of the right method are to be considered: the kind and number of elements to be determined, the matrix and its composition, the form and amount of the sample, the number of samples, the time available and finally the demand on precision.

For combined procedures we also have to meet all demands mentioned before to avoid systematic errors. For decomposition, separation and determination we have only a few different principles, suitable for very low element contents. For instance decomposition can be carried out in a pressure bomb with an insert made of PTFE or glassy carbon (Ref. 2&12). Also the decomposition in the gas phase is unconditionally to be preferred to solution procedures, which renders possible also the separation of easily volatilized elements and compounds from highly volatilized matrices (Ref. 2,4&13). Also liquid-liquid distribution using small test tubes or displacement syringes (Ref. 3) or the displacement exchange (Ref. 14) as well as electrolytical deposition (Ref.3&15) can be used.

EXAMPLES OF COMBINED PROCEDURES FOR EXTREME TRACE ANALYSIS

Electrolytic preconcentration of trace elements (e.g. Hg, Cu, Bi, Pb, Cd, Fe, Ni, Co, Zn) occurring in non-deposited matrix elements (e.g. Be, Zr, Nb, W) can be achieved quantitatively within a short time from a fairly large electrolyte volume (about 50 ml) if the mass transport in the electrolyte is not effected by stirring of the solution or rotation of the cathode, but by means of a hydrodynamic system (Ref. 15). Figure 12 shows the apparatus in which



1 electrolyte storage vessel (PTFE, ca. 70ml)
2 graphite tubing cathode (length 9mm, od = 5mm, id = 2.8mm)
3 mounting for anode and cathode
4 Pt-Ir-anode
5 PTFE-pump
6 power supply
7 pumping circuit
8 anode guide
9 Pt-contact

Fig. 12. Electrolysis in the hydrodynamic flow system.

the electrolyte is circulated rapidly, by means of a PTFE pump, through a small graphite tube serving as cathode. The platinum-iridium-anode runs concentrically through the cylinder.

The distance between cathode and anode of 0.7 mm allows electrolysis with high current density of about 1 A/dm^2. By this and the high circulation rate (20 ml/min), the interferences caused by hydrogen evolution is avoided and the yields are better than 98 %.

The metals deposited inside the cathode tube can be determined directly by, for example INAA or ETA-AAS where the tube is used directly as a furnace (Fig. 13). The elements, evaporated by heating the graphite tube can also be transferred into a microwave induced argon plasma (MIP-OES) (Fig. 13), the quartz capillary of which is attached directly to the tube (Ref. 16). The elements are excited simultaneously yielding detection limits as low as 1 ng.

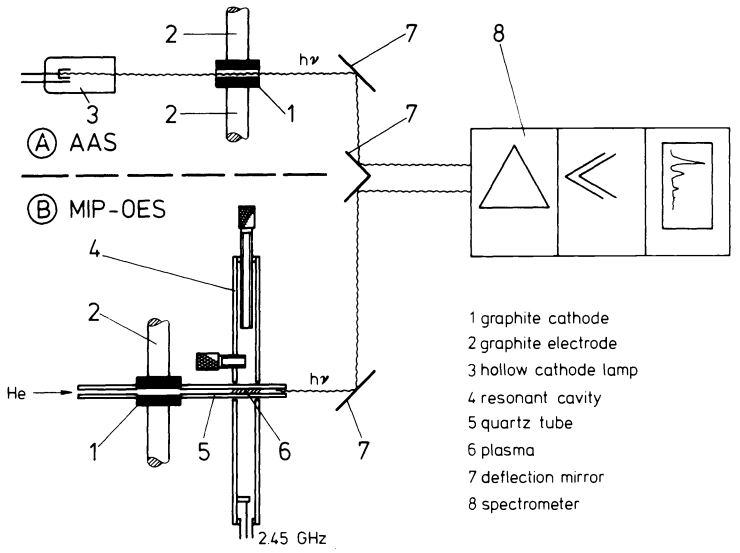


Fig. 13. Determination of traces of elements by AAS or OES after electrolytical deposition inside a tubular graphite cathode.

As an ideal example, the determination of mercury (Ref. 17) in the ng- and pg-range in most of the inorganic and organic substances may be mentioned (Fig. 14). The sample is decomposed in a closed quartz tube system by micro-

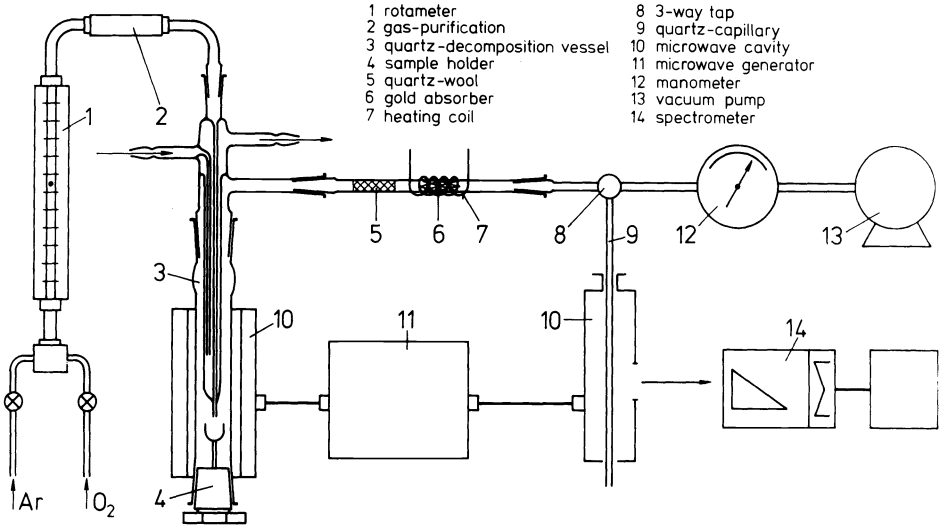


Fig. 14. Decomposition of biological matrices and rocks in a microwave induced oxygen plasma and determination of mercury in a microwave induced argon plasma.

wave induced oxygen expelling the mercury and collecting it on a gold absorber system. Heating up this system in an argon atmosphere, the isolated mercury can be determined way down to the pg-range by an OES/MIP-technique with only a very small systematic error. A similar volatilization method can be used for the accurate determination of selenium in highly pure metals.

With these examples I wanted to show some of the tricks of a big list, by which the requirements of the extreme trace analysis summarized in this report can be met. Of course there are a lot of other possibilities in this field which could not be reported here. A lot of work has to be done until the main aim will be reached, to have prepared all the standard reference materials we need and to use also the much more simpler and more comfortable direct instrumental procedures for routine work in extreme trace analysis of the elements.

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