SOME ADSORPTION/CONTAMINATION PHENOMENA OBSERVED IN DILUTE TRACE ELEMENT SOLUTIONS STORED IN HIGH-DENSITY POLYETHYLENE CONTAINERS.

Hydrogeochemical sample collection in the Karroo.

(J.W. Marchant)

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By

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ABSTRACT

A review of the Literature reveals that the concentration of trace metals in natural water samples can be radically altered by adsorption/contamination phenomena within the storage vessel, and that container pre-cleaning and sample acidification and freezing are advisable.

Experiments were devised or modified to test whether the locally-produced Polykan 57/500 high-density polyethylene containers were suitable for the storage of aqueous trace element samples which were to be collected in the Karroo Uranium Groundwater Hydrogeochemical Prospecting Project. In these various experiments some or all of the elements Cd, Zn, Tl, Pb, Mn, Ag, Cu, Co, Cr, Fe and U were determined by either AAS, DNC or gamma-ray spectrometry. The container components (1) bakelite cap, (2) cardboard liner and (3) polyethylene bottle were analysed (low-temperature RF ashing effectively used to destroy (3)) and were found to contain (ng/g):

(1) Cd 30, Zn 11895, Tl 4, Pb 347, Mn 10153, Ag 1,2 Cu 156, Co 187, U <300.

(2) Cd 21, Zn 159903, Tl 25, Pb 559, Mn 5721, Ag 0,6, Cu 252, Co 99, U <300.

(3) Cd 3, Zn 883, Tl 0,8, Pb 11, Mn 12, Ag 0,1, Cu 0,7, Co 1,3 U <300.

The analysis of pure water and HCl or HNO_3 solutions stored in these containers for eight weeks or more showed that Zn (31 to 226 µg/l) and Mn (20 to 75 µg/l) were the only serious contaminants and that they came from the closure and not the polyethylene.

Radio-isotopic studies showed that none of the element solutions studied (Zn 0,15 to 1,0 µg/l; Cr 0,74 to 4,44 µg/l; Fe 3,4 to 126,8 µg/l; Co<0,192 µg/l) were appreciably (<10%) adsorbed onto the polyethylene from HCl, HNO_3 or $HClO_4$ solutions after 64 days.

After eight weeks of storage, the following changes were noted in trace element solutions stored in various acid media:

Original concentrations (µg/l) : Cd 5, Zn 5, Tl 50, Pb 10, Mn 10, Ag 5, Cu 10, Co 20.
HNO_3: no measurable changes.
HCl: % loss: Tl 87.
$HClO_4$: % losses : Cd 55, Tl 97, Pb 20, Mn 50, Ag 55, Co 18.

Infra-red spectroscopic analysis showed that concentrated $HClO_4$ apparently did not change the surface properties of polyethylene, but that HCl and HNO_3 produced unexplained changes. Electron photomicrographs showed no visible changes.

It is concluded from this and cited work that the Polykan containers are acceptable for the storage of given trace element samples provided that (i) The solutions are isolated from the closure by polyethylene sheeting (ii) The container is pre-cleaned for 24 hours with 10% HNO_3 (longer or stronger may alter the plastic surface) (iii) The sample is acidified to pH 1,0 with very pure HNO_3 and preferably frozen.

Additional study showed that after four years of storage in Consul 0222 high-density polyethylene containers, pure water and nitric acid solutions showed the following maximum concentrations of contaminants (µg/1): Fe 0,4; Cr 0,6; Ni 1,0; Tl 0,6; Co 1,5; Mn 0,14; Ag 0,17; Cu 1,5; Cd 0,17; Pb 2,4; Zn 2,4.

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1. PREAMBLE.

With the advent of modern analytical techniques such as neutron activation methods and flameless atomic absorption spectrophotometry, which are capable of detecting nanogram masses of many elements, the problem of analytical sensitivity has, in many cases, become of less concern than the control of sample representativeness. Several conditions must be met before an analysed sample can be regarded as representative, one of them being that the composition of the sample does not change in an uncontrolled manner between collection and analysis. This particular difficulty is of special concern to the geochemist involved in the analysis of sub-milligram masses of elements in water samples, and this thesis is concerned specifically with the degree to which the Hydrogeochemical Sample can be modified by the container in which it is collected and stored. Most of the text of this thesis deals with an investigation of the relevant characteristics of a specific type of polyethylene container presently in use for sampling in a uranium hydrogeochemical exploration project.

2. AN INVESTIGATION OF THE SUITABILITY OF A GIVEN TYPE OF POLYETHYLENE CONTAINER FOR THE COLLECTION AND STORAGE OF VERY DILUTE SOLUTIONS OF VARIOUS TRACE ELEMENTS.

2.1 INTRODUCTION.

A large contribution to uranium exploration in South Africa is presently being made by the Geological Survey of South Africa, which has concentrated its activities in the Karroo, an area with good uranium potential /69/. As part of the regional survey of this area, hydrogeochemical samples are being collected and analysed for major and trace elements. The object of the experiments recorded in section 2 of this thesis was to determine whether the Polykan 57/500 polyethylene containers tentatively selected by the Geological Survey are suitable for the collection and storage of water samples in which certain trace elements are to be determined. Throughout this section the selection of the elements to be analysed, the acids used as preservatives, and experimental techniques were governed by the practical requirements of this hydrogeochemical survey.

2.2 THE PROBLEM OF STORAGE AND PRESERVATION OF VERY DILUTE SOLUTIONS OF METALS AS DESCRIBED IN THE LITERATURE.

"Natural water is outstandingly susceptible to contamination"

(Hawkes /20/, p. 547)

Workers involved in the determination of trace metals in natural aqueous solutions (eg. Hem /17/, Hawkes and Webb /18/) are generally agreed that there are two principal potential problems involved in the storage and preservation of such solutions prior to analysis. One problem is that of contamination of the sample by the container itself during storage* /17,18,19/; the other is that of loss of trace elements from solution as a result of mechanisms such as immobilization of these elements on container surfaces, or

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* (as opposed to contamination from extraneous sources prior to and during analysis, which is a separate problem.)

precipitation, volatilization, etc. (/27-40/).

The problem of contamination of water samples by sample containers is an old one. For example, Turner /1/ stated (p.213): "The fact that water is capable of attacking glass was known long ago. It has not been considered necessary, however, to quote any earlier authorities than Scheele /2/ and Lavoisier /3/, in the second half of the eighteenth century. For the reader who is interested in the history of the subject, it may be mentioned that Lavoisier, in his memoir on the subject, makes reference to the observations of several earlier experimenters." Cauwood *et al.*/4/ also mentioned the work of Lavoisier (p.154): "Lavoisier, the first chemist who, after Black, based his deductions on quantitative experiments, came early into contact with the problem of the corrosion of glass surfaces. When water was boiled for a considerable period in glass vessels a distinct amount of solid matter collected, and the explanation commonly given, on the basis of the old Greek philosophy, was that water had been turned into earth. Lavoisier proved that the earthy matter observed was accounted for by the attack of the water on the glass, which had lost weight in the process."

Numerous papers on the topic of the durability of glassware had appeared before about 1923 (eg. /5 to 16/). Recent writers have investigated both glass and plastic containers for sample storage purposes. There was a time when many workers (eg. /17, 18/) hailed polyethylene bottles as contamination-free, but this euphoria has long-since been dispelled. For example, Orren /21/ found that certain polyethylene bottles slowly released relatively large quantities of zinc into solution, despite previous decontamination procedures (soaking in both water and in hot or cold dilute (between 2N and 8N) hydrochloric acid and a thorough rinse with double-distilled water). The use of Teepol* detergent in boiling 6N hydrochloric acid reduced the amount of zinc released by about 50%, but boiling for two hours did not further reduce zinc release. "This suggests the possibility that the zinc was not present only as a surface contaminant, but was perhaps distributed throughout the bulk of the material, and slowly diffuses out" (Orren /21/).

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*Registered trade name.

Levinson /19/ and Orren /21/ recommended that all containers for water samples should be viewed as potential sources of contamination. The former author suggested that all new bottles should be cleansed with a strong metal-free acid before being used. Bottles which had previously contained metal-rich samples were not to be used subsequently for collecting and storing water samples. Other types of containers which were to be avoided included all low-density and all coloured polyethylene bottles. Clear, high-density polyethylene containers are suitable, even if the walls are relatively thin.

Rainwater and Thatcher /22/ indicated that much work will be involved in an evaluation of all the factors germane to the selection of containers used to collect and store water samples. Some of the merits and demerits of a wide range of container types, including hard rubber, polyethylene, glass and other plastics, were discussed. It was suggested that all new bottles should be thoroughly cleansed before use, filled with water, and allowed to soak for several days to remove water-soluble material from the container surfaces. They observed that many of the common container closures (lids or caps) have liners (eg. waxed paper or cork) that may be sources of trace metals.

A wide variety of solvents, containers, reagents and other materials normally used during trace element analysis of sea water were evaluated by Robertson /23/ in terms of trace element contamination of samples contacting these materials. All rubber materials were found to contain significant (0,3% to 4%) amounts of zinc. Teflon* appeared to be relatively free from trace metal impurities and could therefore be recommended for use as containers, but high cost prohibits everyday, large-scale usage of this material. With the exception of iron, polyethylene bottles generally contained low concentrations of all the trace elements studied. Polyethylene bottles therefore appeared to be the most satisfactory material for the storage of aqueous samples, and superior to glass bottles, which contained relatively large amounts of zinc, hafnium, scandium, cobalt, antimony and arsenic.

In a similar type of study, Scott and Ure /24/ evaluated the

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* registered trade name for polytetrafluoroethylene.

contamination from some extraneous sources prior to and during chemical analysis. The results indicated that Ti, Ba, Cd, Zn and possibly Mn were present at concentrations of more than 1% in the ash of some of the materials studied, which included various types of polythene, polypropylene, PVC, perspex, polystyrene, nylon* , teflon, bakelite*, silicone rubber and various adhesive tapes. The determination of elements extracted from screw-on tops of glass bottles and their associated cardboard liners by cold dilute nitric acid in a period of twelve hours indicated that Cu, Fe, Mn and Zn could be introduced in significant amounts (up to 0,2%) into samples contacting these materials.

Contamination of water samples stored in containers can also result from the leaching of trace elements which were adsorbed onto the container surfaces from previous samples stored in that container, and even from certain cleaning solutions used to wash the container. For example Laug /25/ has shown that the use of a H_2SO_4-$K_2Cr_2O_7$ cleaning mixture can result in the adsorption of dichromate on glass surfaces and that Cr may leach into samples which are stored in containers previously cleaned with the mixture. The adsorption was found to occur relatively rapidly during initial contact with the cleaning solution, with a subsequent decrease in the rate of adsorption with time. Hot water removed the adsorbed dichromate better than cold water.

Further evidence of the leaching of previously adsorbed elements like sodium and cesium from glass was reported by Long and Willard /26/. It was found that, under the appropriate respective conditions, the rate of desorption of sodium from glass surfaces was approximately the same as the rate at which it had previously been adsorbed.

Chao *et al.*/27/ suggested that containers be soaked in strong nitric or hydrochloric acid for some days before re-using them to collect new samples, in order to reduce the possibility of cross-contamination between samples. It was also suggested that samples be acidified to a low pH value (about 1) at the time of collection to prevent the adsorption of trace elements (such as silver) onto container surfaces. Naturally, the

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* registered trade name.

minimization of adsorption also minimizes the risk of cross-contamination of subsequent samples collected in the same containers.

Eichholz *et al.* /28/ suggested that contaminating "films" on container surfaces could affect surface phenomena to various degrees, and that contamination measurements were therefore valid only for the particular combination of solutions, materials and surfaces involved during any specified cleaning procedure. These authors also note that new glass and plastic containers from the same supplier or even the same batch can show large differences in surface phenomena even when handled and pre-treated in an identical manner. These factors are considered to be largely responsible for the discrepancies in results reported by various workers.

Struempler /29/, too, suggested that various container types exhibit variable surface properties when he stated (p.2254) that "contamination effects associated with the analytical environment and the stabilization of ions in solution are variables which must be largely resolved on an individual basis". During a study of the adsorption, from aquatic samples, of the elements silver, cadmium, lead, zinc and nickel onto glass, polypropylene and polyethylene container surfaces, Struempler /29/ also stated that no single container type proved satisfactory for storing all types of ions in dilute solutions of below 10 µg/l concentration. New polypropylene containers could not be cleaned satisfactorily enough to remove all traces of cadmium and zinc. Apparently the materials used during the manufacture of certain types of containers can be a source of serious contamination. Polyethylene containers appeared to be the most satisfactory, while glass containers were found to be unsuitable.

Riley /30/ has suggested several reasons for the adsorptive properties of glass and plastic surfaces. The most important of these is that, since these materials are supercooled liquids, they possess high adsorption energies due to distorted and broken bonds. This free energy is reduced by the formation of bonds between the surface and the adsorbed ions. In this manner, glass can act both as a cation and anion exchanger. By way of contrast, the surfaces of plastics may become degraded under the influence of oxygen, heat,or light, with the formation of carboxyl or carbonyl groups having adsorptive properties. Catalysts, fillers and plasticizers present in plastics may also offer active sites for adsorption.

Robertson /31/, using radioactive tracers in a study of the adsorption of trace elements in sea water onto glass and polyethylene surfaces, found that serious losses of indium, scandium, iron, silver, uranium and cobalt occurred. Indium was lost most rapidly, with greater than 90% adsorbed onto polyethylene surfaces after about 20 days of storage. However, when the pH of the sea water was lowered to about 1,5 with hydrochloric acid, the adsorption onto polyethylene was completely eliminated. Indium was slowly adsorbed from the sea water onto glass surfaces, with about a 20% loss after 75 days of storage. The behaviour of iron and scandium was quite similar to that of indium, except that the addition of hydrochloric acid only partially prevented the adsorption of scandium on polyethylene. About 20% of the uranium present was lost to glass surfaces and about 10% to polyethylene surfaces after 50 days, despite the addition of hydrochloric acid to the sea water. However, HCl prevented the adsorption of silver and cobalt onto polyethylene surfaces. Negligible adsorption of zinc, cesium, strontium and antimony on all container surfaces was observed for storage periods of up to 75 days. It was recommended that polyethylene bottles be well rinsed before use with purified hydrochloric or nitric acid to remove traces of iron or other materials on the surfaces of the bottles. It was also suggested that freezing the acidified samples might retard the adsorption of scandium and uranium onto polyethylene surfaces.

West *et al.* /32a,b/ found that serious losses of silver ("49% to 140%" onto pyrex glass and 40% to 79% onto polyethylene) occurred under uncontrolled conditions, but that this could be prevented by the use of a complexing ligand such as sodium thiosulphate at a concentration of 0,1 M. The amount of silver adsorbed onto glass at a pH of 4 was markedly higher than that at pH values of 7 and 8. This contradicts the observations of other workers eg./27,33,34/, who found a direct(but not necessarily linear) relationship between pH and the amount of silver adsorbed on glass surfaces.

Durst and Duhart /38/ used an ion-selective electrode to study the adsorption of silver on Vycor*, polyethylene, teflon, Desicoted** pyrex*and pyrex surfaces during a test period of up to 46 days. It was found that between 10% to 15% of the original concentration of silver was lost during the first 24 hours of contact with pyrex and desicoted pyrex materials. During this period, about 5% adsorption occurred on polyethylene surfaces, while teflon surfaces adsorbed less than 2% of the original amount of silver. Adsorption levels at the end of 46 days increased in the order: vycor<polyethylene≈teflon<desicoted pyrex<pyrex; ranging from 43% adsorption for vycor to 59,5% for pyrex. It appeared that the greatest differences in adsorptivity were exhibited by the different types of materials within the first two or three days, while after longer periods the rates of adsorption became roughly equal. It was concluded that none of the materials tested was satisfactory for storage of untreated dilute solutions of silver for longer than one day, and although the effect of various preserving agents was not investigated, it was suggested that the addition of a chemical stabilizer such as thiosulphate was essential for the prevention of losses of silver by adsorption.

Chao *et al.*/35/ found that adsorption of gold from new one-litre polyethylene containers which had been washed with 3 N hydrochloric acid and thoroughly rinsed with distilled water before use, could be prevented throughout a test period of 21 days by three methods: (1) acidification of the test solution to pH 1 with hydrochloric acid and addition of between 5 to 50 mg/l of bromine, (2) acidification with hydrochloric acid to 1 N without addition of bromine, and (3) acidification with nitric acid to 2 N or 3 N. Acetic acid was not effective in preventing gold adsorption on container walls, since about 80% of the metal was lost from solution after 10 days of storage at pH values of 2 and 3.

Hinkle and Learned /36/ found that mercury was adsorbed onto polyethylene container surfaces soon after sample collection.

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* registered trade name.

** Desicote is a registered trade name.

A water sample which had been stored for one month in a polyethylene bottle showed a tenfold decrease in mercury concentration. Upon the container being emptied and washed four times with 1 N hydrochloric acid, the wash solutions still contained significant quantities of mercury desorbed from the inner surfaces. In comparison, a new polyethylene bottle of the same type yielded no mercury after each of four equivalent washings.

Toribara *et al.*/37/ showed that a loss of radioactivity from labelled mercury II solutions was due to reduction of some mercury II by reducing agents present in solution, followed by disproportionation of mercury I and the loss of metallic mercury to the gas phase. It was found that this loss could be prevented by the addition of a small excess of an oxidant such as permanganate.

The loss of mercury from dilute solutions stored in polyethylene containers under routine conditions of sample collection, the effective storage of such solutions and measurement of Hg in them by atomic absorption spectrophotometry (using a cold vapour method) were studied by Coyne and Collins /39/. Sixty percent of the mercury spike added to an unpreserved sample was lost before the first analysis could be made. The loss continued with time, and within three to five days nearly all the added mercury was gone. When acetic acid/formaldehyde (10:1) was used as a preservative, about 20% of the added mercury was immediately lost, and only about 50% remained after three days. After twenty days almost no mercury was detectable in the preserved sample. The effects of hydrochloric-, sulphuric-, phosphoric- and nitric acids as preserving agents were also studied. Only nitric acid (10 ml. per litre of sample ≡ (pH 1)) was found to be an effective preservative. However, it was also found that the acid had to be present in the container before the water sample was introduced in order to achieve maximum efficiency in preventing adsorption.

Rosain and Wai /40/ monitored mercury losses from solutions stored in polyethylene, PVC and soft glass bottles. The containers were pre-cleaned by scrubbing with soap and water and soaking overnight in sulphuric acid/ dichromate cleaning solution, followed by rinsing with distilled water, aqua regia, and a final rinse with distilled water. It was found that, at pH 7, the rate of loss of mercury followed an exponential decay curve, with losses of about 50% occurring after 100 hours. After 400 hours, the losses were about 80%. These data suggested that the loss of mercury followed first-order kinetics. No recommendations were made as to the most satisfactory type of container, except that PVC appeared to be less satisfactory than polyethylene or glass, which showed similar characteristics. However, it was recommended that samples be acidified to a pH of less than 0,5 immediately upon collection, and that they be analysed as soon as possible.

In a similar study, Feldman /41/ found that distilled water solutions containing 0,1 to 10,0 ng Hg/ml lost a substantial fraction of the element if the samples were untreated, or even if they contained HNO_3, $H_2SO_4/KMnO_4$ or $K_2Cr_2O_7$ as preserving agents. These solutions were stored in glass and polyethylene containers for a test period of up to 5 months. It was found that mercury solutions stored in polyethylene containers and treated with 5% (v/v) HNO_3 + 0,05% $Cr_2O_7^{2-}$ were practically unchanged for at least ten days. Solutions stored in glass containers and treated with 5% (v/v) HNO_3 + 0,01% $Cr_2O_7^{2-}$ stayed at full strength for the maximum period of five months. However, it was conceded that this treatment might not necessarily be effective in preserving all concentrations of all elements, and that precautions adopted in specific cases would have to be chosen in accordance with the relevant special conditions.

Some recent work by the author on trace element contamination of water and nitric acid solutions is in press (Marchant and Klopper/79/). Unfrozen samples of pure water and 10% v/v nitric acid, stored in acid-cleaned linear (high-density) polyethylene containers, are used as contamination blank controls for hydrogeochemical samples preserved by deep-freezing in similar vessels. After four years the maximum levels of metal contaminants in these blanks are (in µg/l): Fe 0,4; Cr 0,6; Ni 1,0; Tl 0,6; Co 1,5; Mn 0,14; Ag 0,17; Cu 1,5; Cd 0,17; Pb 2,4; Zn 2,4. Values slightly lower than these are found for Co, Mn, Ag, Cu, Zn and Pb in the pure water samples. Approximately 0,5 - 1,0 µg/l of both Zn and Pb are derived from the nitric acid.

2.3 METHODS ADOPTED/MODIFIED/DEVELOPED IN THIS INVESTIGATION OF THE PROBLEMS OF STORAGE OF AQUEOUS TRACE ELEMENT SAMPLES.

2.31 INTRODUCTORY SUMMARY.

The following techniques were investigated and are described in detail in respective subsequent sections. In the first instance the suitability and practicability of each method was studied. Where appropriate, the following abbreviated codes summarize the elements analysed and/or the technique used:

Code Group A = Cd, Zn, Tl, Pb, Mn, Ag, Cu and Co by atomic absorption spectrophotometry (AAS).
Code Group B = U by delayed neutron counting (DNC).
Code Group C = Cr, Co, Fe and Zn by gamma-ray spectrometry.

(1) The determination of the concentration of trace elements within the walls of the given type of polyethylene container, and in the bakelite cap and associated cardboard liner. (Code Groups A and B).

(2) A study of the trace element contamination of practically metal-free (sub-microgram per litre levels) water and dilute acid solutions stored in the given type of polyethylene container for various periods up to four months. (Code Groups A and B).

(3) A gamma-ray spectrometric study of the trace element adsorption characteristics of the given type of polyethylene container using radioactive tracer isotopes for monitoring changes in concentration with time. (Code Group C).

(4) A study of the behaviour of very dilute (5 µg/l to 50 µg/l) solutions of various elements stored in the given type of polyethylene container. (Code Group A).

(5) Investigation of the surface properties of the polyethylene by infra-red spectroscopy and electron microscopy.

The containers used in this experimental work were taken from a test batch supplied by the Geological Survey of South Africa. These clear, high-density polyethylene containers (Polykan 57/500, manufactured by Polykan Containers Ltd., Johannesburg) have a capacity of 500 ml, and have a hard black bakelite screw cap with a cardboard sealing liner. Additional technical information about these containers is given in Appendix 1.

2.32 THE DETERMINATION OF THE TRACE ELEMENT CONTENT OF THE GIVEN POLYETHYLENE CONTAINER, THE BAKELITE CAP AND ITS ASSOCIATED CARDBOARD SEALING LINER BY AAS/DNC.

2.321 INTRODUCTION.

It is logical to begin any contamination study of this type by analysing the material of the container. Clearly, only those elements which are present in significant amounts in the material can be regarded as potential contaminants. However, it does not follow that every element which <u>is</u> present in significant amounts will necessarily contaminate the sample. It is possible that some elements may be permanently bound within or onto some or all of the components of the container, and will therefore not be available for transfer into the water sample. The experiment described here is not capable of determining what one might loosely term the "transferability" of trace contaminants, but this question will be taken up again in subsequent sections.

The elements selected for investigation by AAS were: cadmium, zinc, thallium, lead, manganese, silver, copper and cobalt. Uranium was determined by the Atomic Energy Board at Pelindaba, using a delayed-neutron counting method developed specifically for use with geological materials /59a,b/.

2.322 EXPERIMENTAL METHOD.

(a) Preparation and AAS analysis of bakelite cap and cardboard liner samples.

About a dozen bakelite caps (which have a cardboard liner) were removed at random from the supply of polyethylene containers. The cardboard liners were removed by splitting the bakelite caps with a wooden mallet. A wet ashing technique was used to minimize the loss of volatile trace elements. Duplicate samples of each type of material (about 1 gram) were placed in teflon beakers pre-cleaned with hot, concentrated nitric acid, and 20ml of concentrated nitric acid (Hopkin and Williams, Analar Grade) was added to each beaker. The beakers were covered with teflon lids and the contents were evaporated to dryness on an electrical hot plate at a temperature of 60°C. The residue was dissolved in 2 ml of concentrated nitric acid and diluted to a final volume of 50 ml with double-distilled water. These solutions were then analysed directly by flameless AAS, since this technique provides a high sensitivity and detection limits in the µg/l and ng/l range for many trace elements. In addition, small sample volumes are required for analysis.

The carbon rod atomizer, or heated graphite furnace as it is also called, has been effectively used by various previous workers (eg.: Paus /45/, Segar and Gonzalez /46/, Barnard and Fishman /47/, Edmunds *et al.*/48/, Fernandez and Manning /49/) to determine trace elements directly in aqueous samples without the need for prior concentration of these elements by techniques of solvent extraction, ion-exchange or co-precipitation. Extremely low detection limits (µg/l and ng/l range) have been obtained, coupled with a high sensitivity and specificity for many trace elements.

Inter-element interferences with the carbon-rod atomizer are quite different from those observed in the various flame AAS systems, in which the interferences are normally of a chemical nature/79/. In the flameless system, inter-element effects mainly cause signal suppression due to gas-phase interaction between the atomic species present and the cloud of condensing elements. Alger *et al.*/77/ and Anderson *et al.*/78/ have minimized inter-element effects by adjusting the path of the light beam so that it passed through a well-defined zone just above the carbon-rod surface.

Another form of interference in flameless AAS is non-atomic absorption, the effects of which have been investigated by several workers, eg: Billings /50/, Kahn /51/, and Manning /52/. It has been found that non-atomic absorption, which results from the absorption of radiation from the hollow cathode lamp by molecular species which absorb the same wavelength as the resonance line of the analyte element, can be separated from the true sample absorption by the use of a continuum source. This type of source may be a hydrogen hollow cathode lamp or a deuterium arc lamp. The absorption measured with a continuum source at the resonance wavelength of the analyte element is essentially only the non-atomic absorption component present in the total sample absorption signal. Specially designed accessories for atomic absorption spectrophotometers which include a hydrogen hollow cathode lamp or a deuterium arc lamp coupled to electronic measurement devices, similar to the unit described by Dick *et al.*/53/, have been used successfully by previous workers to correct sample absorption readings for non-atomic absorption effects.

This analytical procedure was adopted in all the experiments described in this thesis. The instrument used was a Varian Techtron model AA-6 atomic absorption spestrophotometer fitted with a model 63 carbon rod atomizer, a model BC-6 simultaneous background corrector with a hydrogen hollow cathode lamp, and a Hitachi QPD 54 chart recorder. Hollow cathode lamps for all elements except Ag and Cd, which were Perkin-Elmer products, were of standard Varian Techtron manufacture. The instrument was operated in the peak mode, using the standard instrumental parameters and conditions recommended by the manufacturers (Parker /71/; Varian Techtron /72/.

A micro-pipette of 5 µl volume with disposable plastic tips was used for injection of samples into the carbon rod atomizer. Sommerfeld *et al.* /54/ and Benjamin and Jenne /55/ have evaluated trace metal contamination of disposable micro-pipette tips obtained from a number of different manufacturers. It was found that certain tips contributed zinc, iron and copper to the sample in varying amounts. The length of time for which a sample remained in the tip before being injected into the furnace appeared to be the cause of the varying degrees of contamination. Rinsing of the tips with hydrochloric acid and distilled water was suggested in order to prevent contamination of samples subsequently drawn into these tips.

The tips used in this study ("Autopette") are relatively metal-free and have not caused contamination problems in this laboratory (Orren /42/, Marchant /43/). They were therefore not rinsed with hydrochloric acid, but were rinsed three times with the sample to be injected. The technique of injection was such that each sample remained in the tip for the shortest possible time, with nearly constant periods of time elapsing between injection of consecutive samples, thus contributing to the reproducibility of the results.

Analysis of each sample was repeated until three concordant absorbance values were obtained. The mean of at least three values was taken as the final result in each case.

(b) Preparation and AAS analysis of polyethylene samples.

The literature describes the determination of trace metals such as Ti, Al, Fe, Co, Cu, Sn, Sb, Mn, Zn, Pb, Ag, Au, Cd, Ni, and Hg in various polymers. The methods described include: (i) fusion of the polymer (eg. polypropylene) with sodium carbonate at 800°C /61/, (ii) dissolution of polyester, nylon and cellulosics in a hot H_2SO_4/H_2O_2 mixture /62/, (iii) the use of solvents such as methyl isobutyl ketone, dimethylformamide, dimethylacetamide, cyclohexanone and others for decomposing or dissolving polyvinyl chloride, polystyrene, polyamide, etc. /63/, (iv) high-temperature ashing /24/, (v) neutron activation methods /23/,and (vi) analysis of solid materials such as polypropylene and fluorinated hydrocarbon polymer directly in a graphite furnace without dissolving the samples, which weighed between 6 mg and 15 mg /64/.

In the case of polyethylene, the choice of methods is limited*. It is doubtful whether solid high-density polyethylene is amenable to direct analysis by carbon rod AAS, and in any case, the physical size and geometry of the model 63 carbon rod makes it very unsuitable for this purpose.

High-temperature ashing or fusion methods may lead to the loss of some trace elements through volatilization, and are therefore preferably to be avoided. On the other hand, it is probably impossible to wet-ash polyethylene because at low to moderate temperature it is scarcely attacked or effectively dissolved by any practically-usable reagent /60/. However, it is reported that polyethylene is dissolved at high temperatures by decahydronapthalene (decalin), and an attempt was made to dissolve

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*Assuming, as is the case here, that one does not have easy access to neutron activation methods.

polyethylene by refluxing it with decalin (Merck chemical reagent) at 200°C. The material was apparently slightly dissolved, but most of it merely melted and re-solidified as soon as the temperature dropped. It was concluded that under the circumstances the only feasible method available for destroying the structure of the polyethylene prior to analysis was low-temperature dry ashing in a radio-frequency (RF) reactor.

Gleit and Holland /65/ and others /66,67/ have described the use of electrically excited oxygen for the low-temperature decomposition of organic substances. The method involved the excitation of oxygen by a radio-frequency field to cause oxidation of samples placed in a tube through which oxygen was passed. The temperature in the reaction tube remained below 100°C at all times. A wide variety of organic substances was ashed with no significant loss of elements due to volatilization. Exceptions were iodine and gold, which were recovered quantitatively from a cold trap at the outlet end of the reaction tube. Table 1, which is from Gleit and Holland /65/ and Table 2, which is from Lutz *et al.*/67/, show the percentage recovery of a number of elements in a variety of samples subjected to low-temperature RF ashing.

A total of about 5 grams of polyethylene chips was cut from five Polykan 57/500 containers. These chips were soaked overnight in concentrated nitric acid to remove surface contaminants. The polyethylene chips were ashed in a Perkin-Elmer Coleman 40 low-temperature RF reactor, using an oxygen flow rate of between 3 and 5 cc/min. The reactor was operated for about 14 days until the original polyethylene chips had been reduced to fine, white flakes of ash. The ash was weighed, dissolved in 2 ml of concentrated nitric acid, and the solution made up to a final volume of 50 ml with double-distilled water. This solution was analysed directly by AAS, using the carbon rod atomizer. (See section (a) above).

It should be noted that Gleit and Holland /65/ ashed samples for 1,5 hours only (see Table 1), while in this experiment a period of 14 days was required to destroy the polyethylene structure. It was assumed that no losses of trace elements occurred during this period, since percentage recoveries could not be tested experimentally in this case.

Table 1

Percentage recovery of elements after low-temperature RF ashing vs. conventional ashing of organic samples.

(From Gleit and Holland /65/)

		RF discharge, 1,5 hr.		Muffle furnace	
Nuclide	Sample	Boat	Trap and chambers	24 hr., 400°C.	3 hr. 900° C.
Sb^{124}	$SbCl_3$ + blood	99	0	67	9
As^{76}	$HAsO_2$ + blood	100	0	23	0
Cs^{137}	CsCl + blood	100	0	...	..
Co^{60}	$CoCl_2$ + blood	102	0	98	30
Cu^{67}	$CuCl_2$ + blood	101	0	100	58
Cr^{51}	$CrCl_3$ + blood	100	0	99	56
Au^{198}	$AuCl_3$ + blood	70	30	19	0
I^{131}	NaI + filter paper	31	69	...	..
I^{131}	$NaIO_3$ + filter paper	100	0	...	..
Fe^{59}	$FeCl_3$ + blood	101	0	86	27
Pb^{210}	$Pb(NO_3)_2$ + blood	100	0	103	13
Mn^{54}	$MnCl_2$ + blood	99	0	99	79
Hg^{203}	$Hg(NO_3)_2$ + blood	92	8	<1	0
Mo^{99}	$(NH_4)_2MoO_4$ + blood	100	0	100	83
Se^{75}	Alfalfa	99	0	...	..
Ag^{110}	AgCl + blood	72	28	65	21
Na^{22}	NaCl + blood	100	0	...	..
Zn^{65}	$ZnCl_2$ + blood	99	0	100	30

Table 2

Percentage recovery of elements after low-temperature RF ashing of a variety of samples. (From Lutz *et al.*/67/)

Element	Coal	Orchard leaves	Beef liver
Sodium	98	100	104
Magnesium	98	101	95
Aluminum	105	-	112
Potassium	101	106	-
Calcium	99	101	99
Scandium	100	101	-
Titanium	105	99	-
Vanadium	98	-	-
Chromium	99	106	94
Manganese	102	102	105
Iron	96	102	99
Cobalt	108	95	106
Nickel	99	99	-
Zinc	107	102	100
Gallium	91	-	-
Arsenic	110	92	-
Sclenium	99	105	-
Rubidium	98	98	92
Strontium	98	106	-
Zirconium	104	108	-
Molybdenum	93	94	-
Antimony	104	108	-
Cesium	102	104	-
Barium	105	109	-
Lanthanum	107	95	95
Cerium	99	98	100
Europium	98	-	94
Hafnium	96	98	-
Tantalum	109	-	-
Tungsten	97	-	-
Lead	106	97	-
Thorium	103	92	-

(c) Determination of U in the cardboard liners, bakelite caps and polyethylene.

Solid samples of these three materials were prepared for uranium analyses by methods described in the foregoing sections (a) and (b).

Triplicate samples of these materials, each with a mass of about 200 mg (accurately weighed), were sealed in special high-density polyethylene vials with snap-on lids which are routinely used for holding solid samples in the nuclear reactor at Pelindaba /59b/. The technique used for uranium analysis has been described by Smit /59a,b/.

2.323 Results and conclusions.

The results of the abovementioned analyses are given in Table 3. The agreement between the two separate sets of analyses is always reasonable and is often very good. Variations between the duplicates may be due to experimental error or to inhomogeneity in the distribution of particular trace elements in the materials of the container components /28/. Differences may occur between different batches, between indvidual containers within the same batch, or even between different parts of the same material component (eg. polyethylene) of any one bottle. These differences are likely to be greatly reduced if, as is the case here, the samples analysed are composed of fragments taken from several different individual containers. It may be concluded that the mean trace element content of any five Polykan containers selected at random is likely to be roughly constant, and that the data may therefore be used, with a fair degree of confidence, to calculate the "mean" trace element contents of an "average" container (Table 3). These "mean" values will be of considerable use in any attempt to predict which of the trace elements in the containers are (Statistically) likely to cause contamination problems. Unfortunately, the relative constancy of this "mean" does not guarantee that any individual container will have the same trace element content as the next, and it is therefore not reasonable to hope that these "mean" values may be quantitatively related to the level of contamination observed in a water sample stored in any one randomly selected Polykan container.

Table 3

Trace element content of container components.

First determination

		Cd	Zn	Tl	Pb	Mn	Ag	Cu	Co	U
liners	(a)	25	170731	27	599	5335	0,5	275	95	<300
"	(b)	5	34146	5	120	1067	0,1	55	19	<60
caps	(a)	33	13230	5	306	9072	1,0	149	171	<300
"	(b)	139	55566	21	1285	38102	4,2	626	718	<1260
polyethylene	(a)	3	952	1	9	9	0,1	0,9	2	<300
"	(b)	96	30464	32	288	288	3,2	29	64	<9600
total mass	(c)	240	120176	58	1693	39457	7,5	710	801	<10920

Second determination

		Cd	Zn	Tl	Pb	Mn	Ag	Cu	Co	U
liners	(a)	17	149075	23	520	6108	0,7	229	103	<300
"	(b)	3	29815	5	104	1222	0,1	46	21	<60
caps	(a)	27	10560	2	388	11235	1,5	164	204	<300
"	(b)	113	44352	8	1630	47187	6,3	689	857	<1260
polyethylene	(a)	3	815	0,6	13	15	<0,1	0,6	0,7	<300
"	(b)	96	26080	19	416	480	<3,2	19	22	<9600
total mass	(c)	212	100247	32	2150	48889	<9,6	754	900	<10920

Average values

		Cd	Zn	Tl	Pb	Mn	Ag	Cu	Co	U
liners	(a)	21	159903	25	559	5721	0,6	252	99	<300
"	(b)	4	31981	5	112	1144	0,1	50	20	<60
caps	(a)	30	11895	4	347	10153	1,2	156	187	<300
"	(b)	126	49959	15	1457	42643	5,0	655	785	<1260
polyethylene	(a)	3	883	0,8	11	12	<0,1	0,7	1,3	<300
"	(b)	96	28256	26	352	384	<3,2	22	42	<9600
total mass	(c)	226	110196	46	1921	44171	<8,3	727	847	<10920

(a) = concentration in material in ng/g.

(b) = total mass (ng) of element in material, assuming the following mean masses for components of a typical container: cardboard liners = 0,2g; bakelite caps (without liner) = 4,2g; polyethylene = 32g.

(c) = total mass of element in the whole container, assuming the masses given in (b).

It is self-evident that some of the elements listed in Table 3 do not pose a serious threat of contamination. For example, even if all the silver present in all the components of a typical container were somehow to be leached into an aqueous sample stored in that container, the resultant concentration of silver would nevertheless be somewhat less than 0,02 µg/l - an abundance which would certainly be regarded as negligible in almost any hydrogeochemical study. Similarly, one may predict that thallium, cadmium, copper and cobalt are unlikely to cause significant problems. Although the mass of lead present is relatively small (about 4 µg/l), it would be unwise to dismiss the possibility of contamination by this element. Zinc and manganese, on the other hand, obviously constitute a potential threat of serious contamination. The closure, rather than the polyethylene, is likely to cause problems. The insensitivity of the analytical method for uranium (in solids) does not allow one to dismiss this element as a potential contaminant of water samples, which are normally analysed by a much more sensitive technique involving pre-concentration by ion-exchange chromatography.

It is concluded that an analysis of samples taken from the components of containers is a useful method of predicting which trace elements are likely to appear as contaminants in liquids stored in those containers. It is probable that the methods described here could be readily combined with a technique such as optical emission spectrography to give a wide coverage of the periodic table.

2.33 THE TRACE ELEMENT CONTAMINATION OF PRACTICALLY METAL-FREE WATER AND DILUTE ACID SOLUTIONS STORED IN POLYETHYLENE CONTAINERS, AS DETERMINED BY AAS/DNC.

2.331 INTRODUCTION.

This experiment was designed to monitor the rate of contamination of either pure water, or solutions of water/HCl or water/ HNO_3 due to leaching of trace elements from the components of the Polykan 57/500 containers. An additional aim of the experiment was to determine whether pre-cleaning the containers with solutions of HCl or HNO_3 had any significant effect on the degree of trace element contamination of samples subsequently stored in them.

The length of the contamination rate test was dictated by the survey described in section 2.1, and specifically by the anticipated delay between sample collection and the analysis of particular trace elements.

A few investigations of this type have been published (section 2.2), but the detailed experimental method used in the present study has apparently not been recorded.

2.332 EXPERIMENTAL METHOD.

(a) Preparation and analysis of samples.

A test batch of seven Polykan 57/500 containers was selected at random from the supply. These were divided into three groups:

(1) two bottles to be pre-cleaned with hydrochloric acid (Merck 'Pro Analysi' Analytical Reagent),

(2) two bottles to be pre-cleaned with nitric acid (May and Baker 'Pronalys' Analytical Reagent).

and (3) three bottles which would not be pre-cleaned with acid but instead rinsed with water double-distilled from quartz*.

The bottles selected to be pre-cleaned with an acid** were filled

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* The water used throughout this study was double-distilled from quartz. The purity of this water is well established (Orren /42/, Marchant /43/).

** Throughout these experiments, the acids used came from the same respective stock bottles.

with a 25% (v/v) solution of the respective acid and were stored on their sides for three weeks to allow for ample leaching of trace elements from all interior surfaces of the containers. The three bottles which were not pre-cleaned with acid were filled with double-distilled water and stored in a similar way to the acid pre-cleaned bottles. After the three-week soaking period, all the bottles were emptied and rinsed five times with double-distilled water.

To one of the bottles pre-cleaned with hydrochloric acid, 5 ml of concentrated hydrochloric acid was added and the container topped up with double-distilled water. The other bottle pre-cleaned with hydrochloric acid was filled with double-distilled water only. In a similar manner, 5 ml of concentrated nitric acid was added to one of the nitric acid pre-cleaned bottles together with double-distilled water. The other bottle pre-cleaned with nitric acid was filled with double-distilled water only.

Of the three bottles which were not pre-cleaned with any acid, one was filled with double-distilled water containing 5 ml of concentrated hydrochloric acid; the second was filled with double -distilled water containing 5 ml of concentrated nitric acid, while the third bottle was filled with double-distilled water only.

For convenience, a flow chart indicating the procedure followed during the preparation of the containers is shown in Table 4.

These samples were then stored lying down on a bench in an air-conditioned laboratory, away from direct sunlight. Most elements were determined once a week for a period of eight weeks. The flameless AAS method used is described in section 2.322(a). In addition, after 12 weeks conventional flame AAS/71, 72/ was used to accurately measure concentrations of Zn, which were too high for the carbon rod method. Uranium was determined only once,*after a storage period of four months. The analysis was performed at Pelindaba by the Atomic Energy Board, using the ion-exchange/DNC method described by Brits and Sunde /73/.

(b) Preparation and analysis of control standards.

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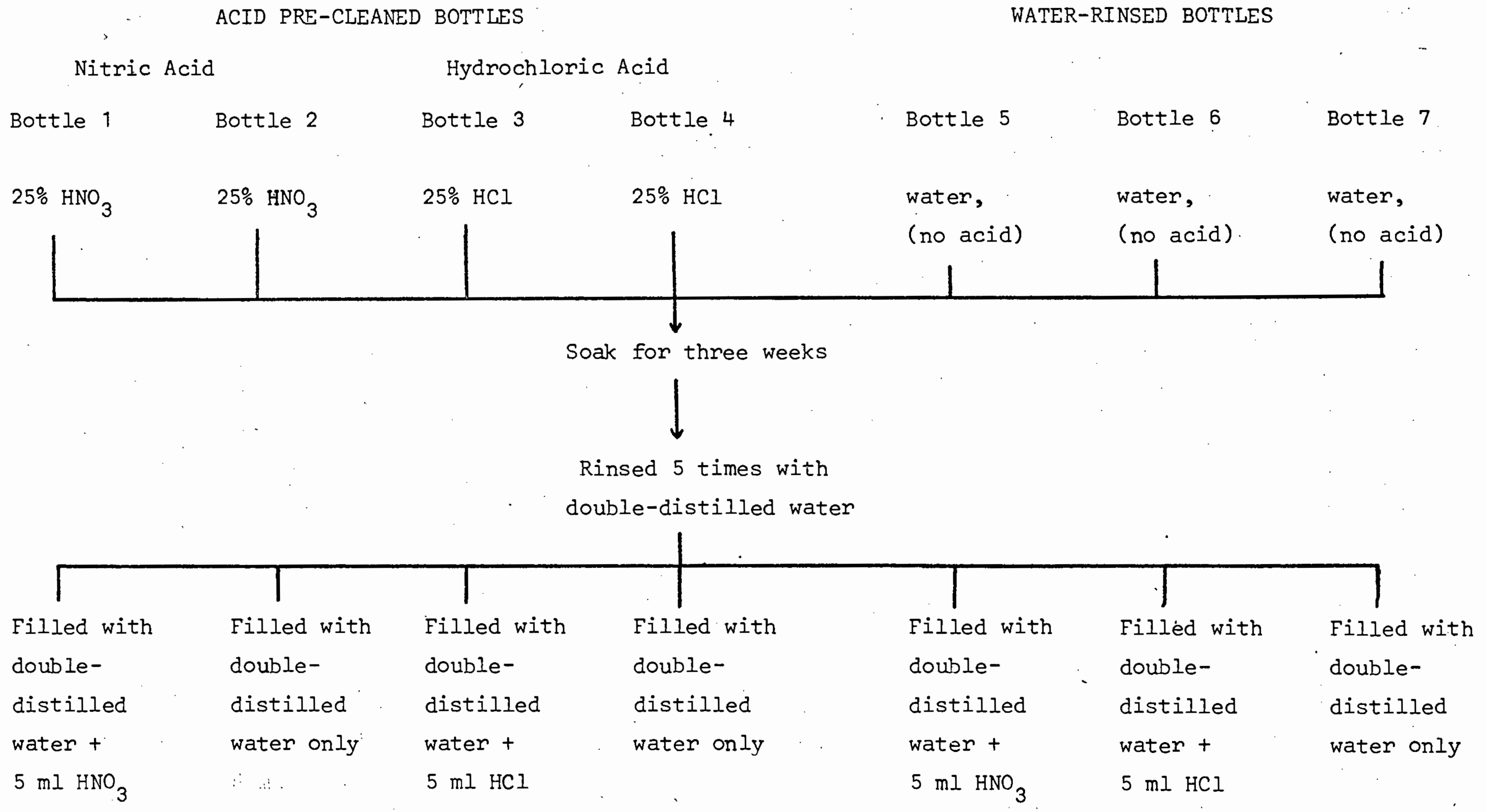
* In terms of the Karroo project, uranium is probably the most important trace element. Therefore, this uranium contamination experiment was later repeated, with slight modifications, because it was essential to verify the conclusions reached in this test. This duplicate experiment is described in Appendix 3. The results of both contamination tests were identical.

Table 4

Flow Chart showing the cleaning and filling procedure for the seven bottles selected for the Contamination Study.



In an experiment of this type, where one anticipates the measurement of concentrations near to the detection limit of the method employed, it is necessary to pay particular attention to the method of standardization in order to ensure that real changes in concentration are not obscured by the severe random variations which are inherent in measurements near the detection limit /70/.

In AAS, two basic techniques of standardization are used, and each has its own advantages and disadvantages. Firstly, there is the technique of standard additions as described by Fuller /44/. It is potentially very powerful, but is used less frequently because it can be time-consuming and is often not strictly necessary. This method involves the addition of a small known amount of a given element to the sample after its original absorbance value has been determined, and obtaining a calibration curve from the difference between the original absorbance value and that observed after the known amount of the element has been added to it. In low-level contamination studies it is obviously not practical to repeatedly add aliquots of the analyte element directly to the sample. To use this technique at all would necessitate the removal of a portion of the sample to a separate container before making standard additions. However, these separate containers constitute a possible external source of contamination, which is to be avoided at all costs. It is therefore apparent that this method of standardization is not suitable here.

The second and more conventional method of standardization or calibration in AAS involves the determination of the absorbance of a number of carefully matched standards of known concentration, followed by the plotting of a working curve of standard absorbance versus concentration values. The concentration of an element in a sample of comparable matrix is then found by reading off from the working curve the concentration corresponding to the absorbance value of that sample. The practical limitation of this method is reached when one attempts to quantify, in the unknowns, differences in concentration which are of the same order of magnitude as the uncertainty in the nominal value of the standard.

When the rate of contamination from sample containers is to be monitored by determining small fluctuations in the same samples over a fairly long period of time, the problem of calibration is accentuated by slight variations in the real concentration of the control standards if these are freshly prepared each week.

To enable a meaningful comparison of week-to-week results to be made under these circumstances, a somewhat different approach to the problem of calibration and the minimizing of week-to-week fluctuations in precision was needed.

The method adopted consisted of monitoring weekly changes in the ratio $\frac{\text{Absorbance value of element X in a sample}}{\text{Absorbance value of element X in a permanent control (standard) solution}}$.

Small variations in absorbance, due, for instance, to week-to-week instrumental drift, should affect both the unknown sample and the permanent standard more or less equally, and should therefore tend to be cancelled out. Since the same permanent standard (control) solutions were to be used throughout the duration of the experiment, their concentrations would have to remain essentially constant during this time. Since the permanent standards are themselves very dilute solutions, they had to be protected as far as possible against potential changes in concentration due to adsorption/contamination phenomena.

It has been shown /42,43,30/ that dilute solutions of most trace elements can be very effectively stabilized by deep-freezing. The standards were therefore kept frozen at minus 20°C at all times other than when they were required for analysis, at which time they were thawed by shaking the bottles in warm water, and afterwards refrozen as soon as possible.

In addition, care was taken to select practically contamination-free containers for the storage of these standards. The vessels selected for this purpose were thick-walled polyethylene bottles which had originally been containers for commercially-supplied, concentrated, high-purity hydrofluoric acid. It seemed improbable that the interior surfaces of these containers would be host to significant amounts of metals. Nevertheless, these vessels were subjected to the following contamination test for the specific purpose of verifying the above assumption:

Double-distilled water was stored in a polyethylene bottle which originally contained hydrofluoric acid, and analysed after two months to determine whether trace metals had been leached from the container surfaces. The results (see Table 5) show that this type of container is practically free of trace metals, and that contamination of the dilute multi-element standard solutions from this source is therefore unlikely. It should be noted that this observation may not hold for other types of samples such as acidified natural water.

The standard (control) solutions were prepared from commercially-supplied stock solutions (1 000 mg/l) of the individual elements. These stock solutions are stabilized with either HNO_3, or HCl or $HClO_4$. In order to prevent the mixing of potential reactants, elements stabilized with different acids were diluted and stored in three separate containers, one for each acid type (see table 6)

A concentration of 5 μg/l of each element, except for Tl which was 100 μg/l, was chosen for the control solutions. For the majority of the elements tested, a volume of 5 μl of the appropriate commercial standard of 1 000 mg/l was added to double-distilled water in glass volumetric flasks which had been soaking in double-distilled water for weeks prior to use. The volume was adjusted to one litre to give a concentration of 5 μg/l for the appropriate elements. For Tl, a solution of 100 μg/l was prepared in the conventional manner by stepwise dilution using carefully cleaned pipettes and volumetric flasks. These solutions were immediately transfered to the HF bottles. The analytical method has been described in section 2. 322 (a)

2.333 RESULTS AND DISCUSSION.

The data obtained from AAS/DNC analysis of the test samples are depicted in Figures 1 to 29, and compiled in tabular form in Appendix 2. The uranium values and those for zinc after 12 weeks of storage only are expressed as accurately-determined concentrations. The remaining data for Zn and for all the other elements are given as both sample/standard absorbance ratios and nominal concentrations. Of the two numbers, the ratio is the better index of change in the solutions, since

Table 5

Contamination test of used HF bottles.

Element	Cd	Zn	Tl	Pb	Mn	Ag	Cu	Co
Initial analysis								
absorbance (x 10^3)	0	11	0	0	0	0	0	0
concentration*	<0,01	0,12	<0,6	<0,2	<0,05	<0,06	<0,5	<0,4
Final analysis								
absorbance (x 10^3)	1	14	0	2	0	0	0	1
concentration*	0,01	0,15	<0,6	0,4	<0,05	<0,06	<0,5	<0,4
Change in concentration*	∿0,01	0,03	zero	∿0,2	zero	zero	zero	∿0,4

* all values in μg/l.

Table 6

Multi-element control standards for AAS analysis.

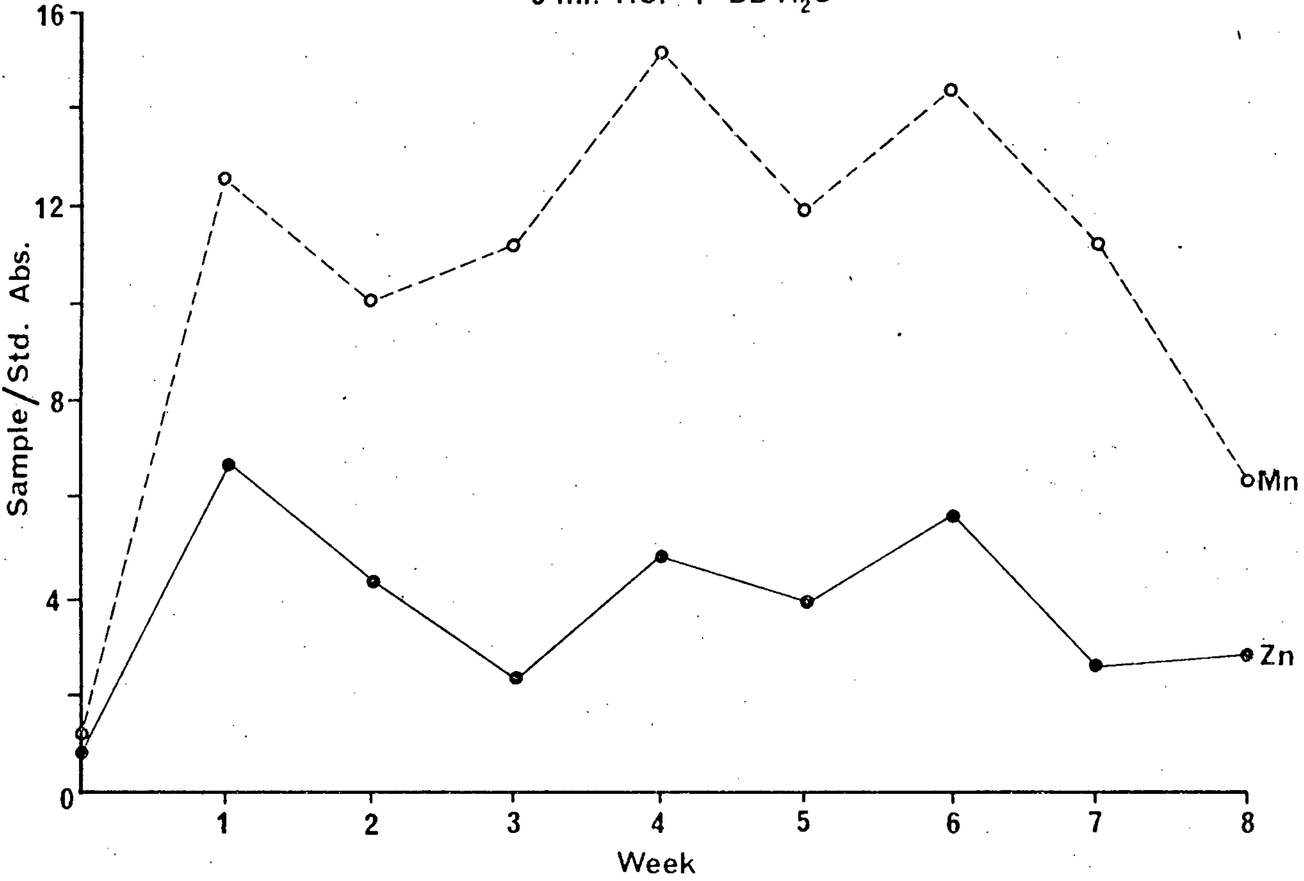
Acid preservative in stock solution	Elements	Final concentration (μg/l)
1 N HNO_3	Ag	5
	Tl	100
1 N HCl	Co	5
	Cu	5
	Mn	5
0,1 N $HClO_4$	Cd	5
	Pb	5
	Zn	5

Figures 1 to 29

Graphical representation of week-by-week sample/standard absorbance ratios for the eight elements investigated in the contamination study described in section 2.33.

FIG. 1

Zn, Mn
HCl cleaned
5 ml. HCl + DD H_2O



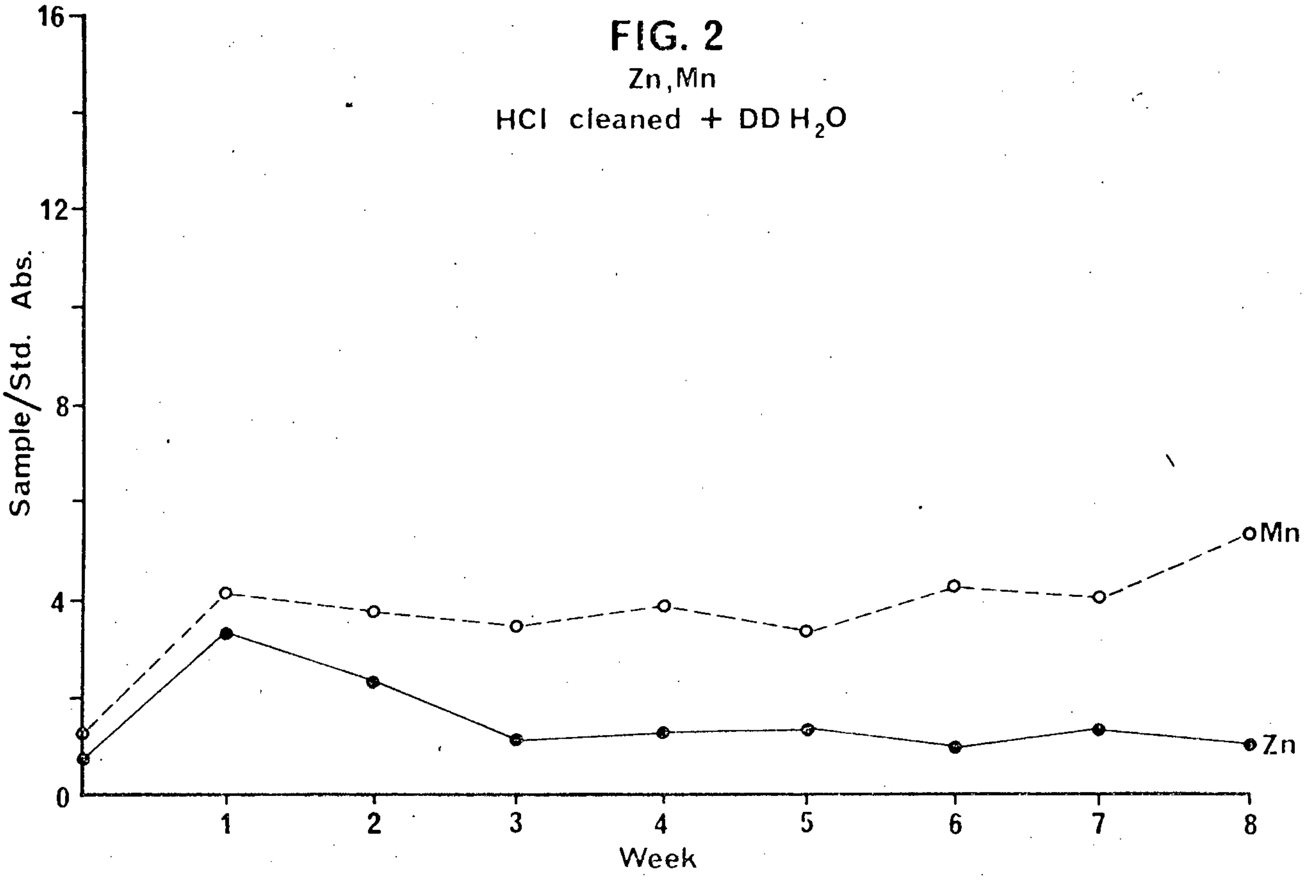


FIG. 2

Zn, Mn
HCl cleaned + DD H_2O

FIG. 3

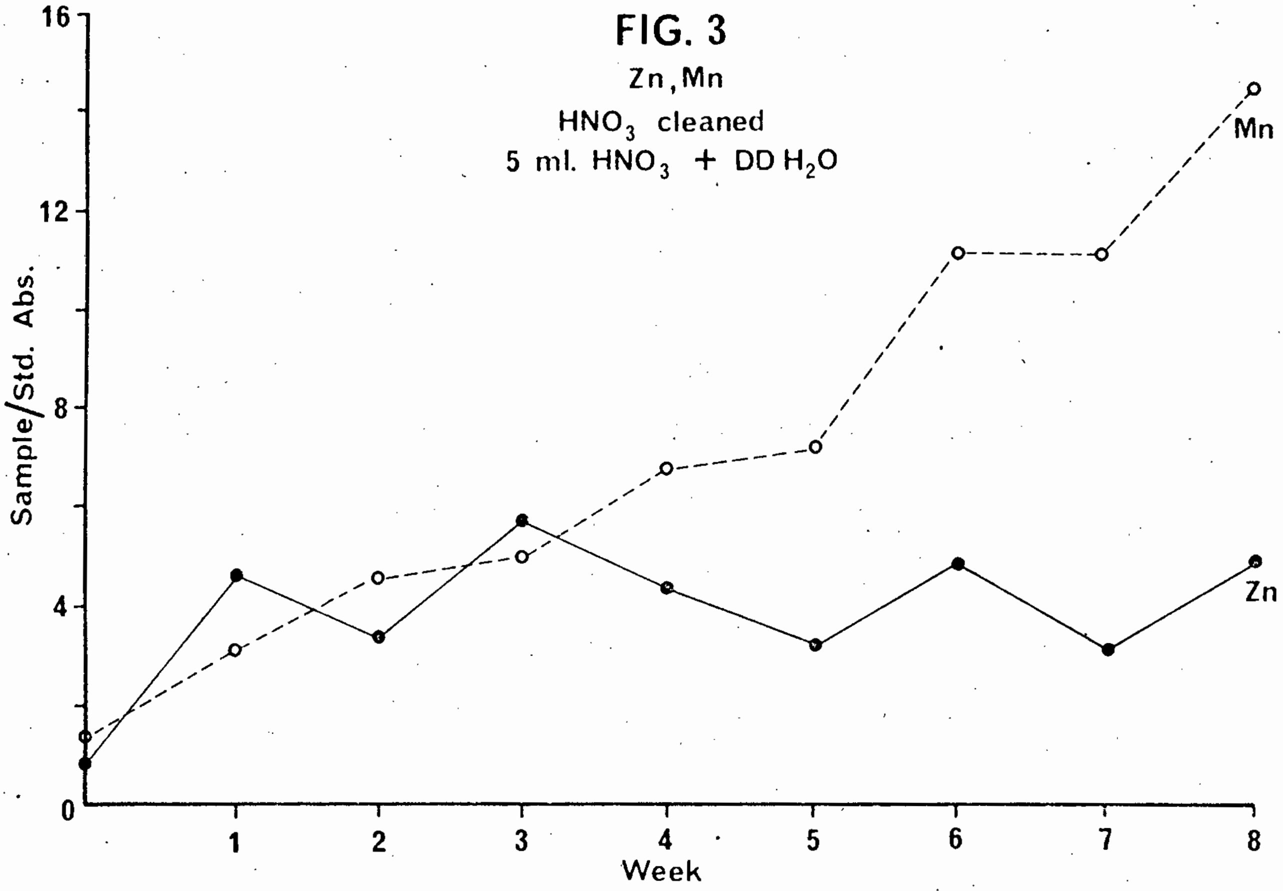
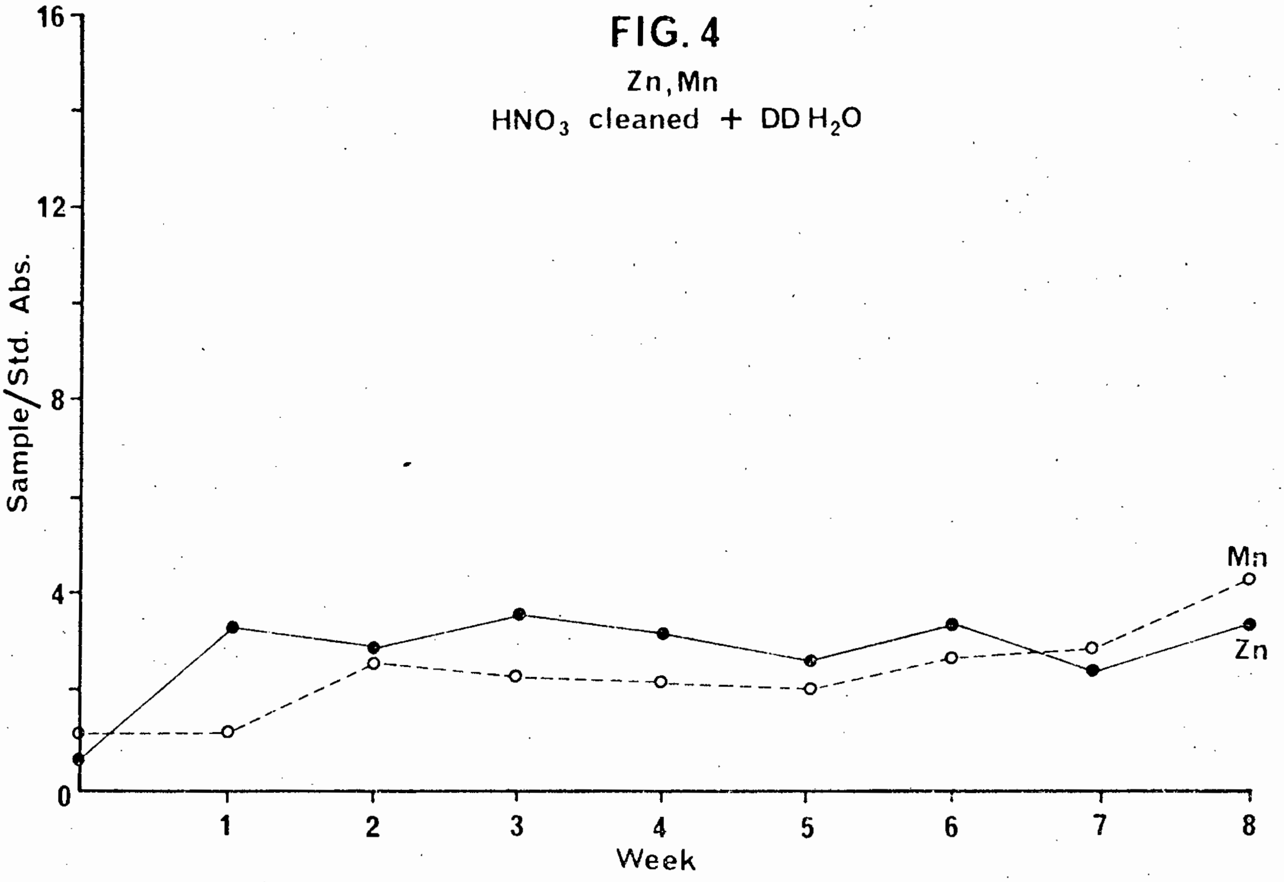

Zn, Mn
HNO_3 cleaned
5 ml. HNO_3 + DD H_2O
Sample/Std. Abs.
16
12
8
4
0
1
2
3
4
5
6
7
8
Week
Mn
Zn

FIG. 4


Zn, Mn
HNO_3 cleaned + DD H_2O
Sample/Std. Abs.
16
12
8
4
0
1
2
3
4
5
6
7
8
Week
Mn
Zn

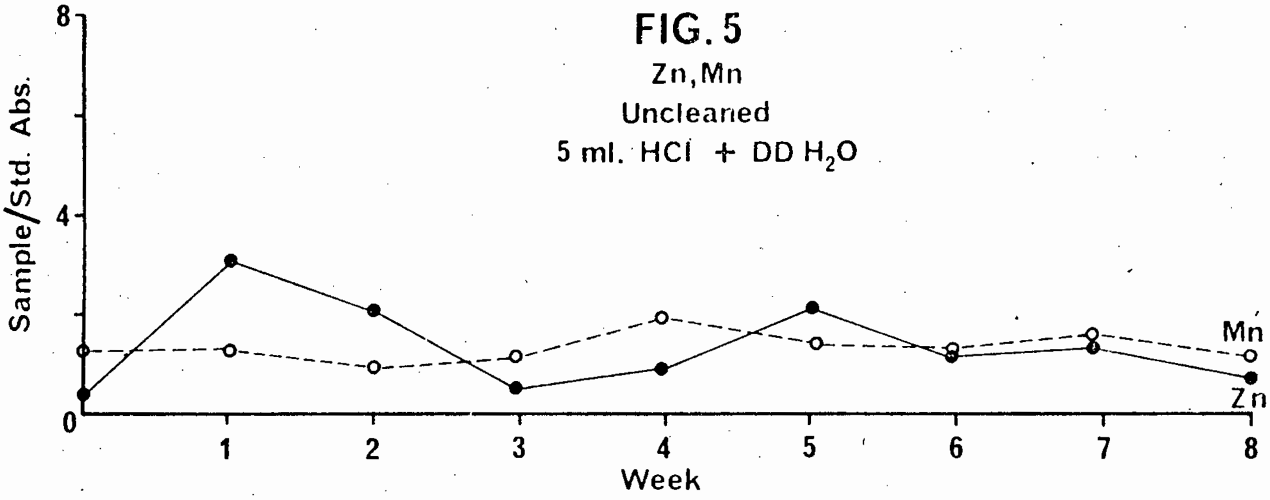


FIG. 5

Zn, Mn

Uncleaned

5 ml. HCl + DD H_2O

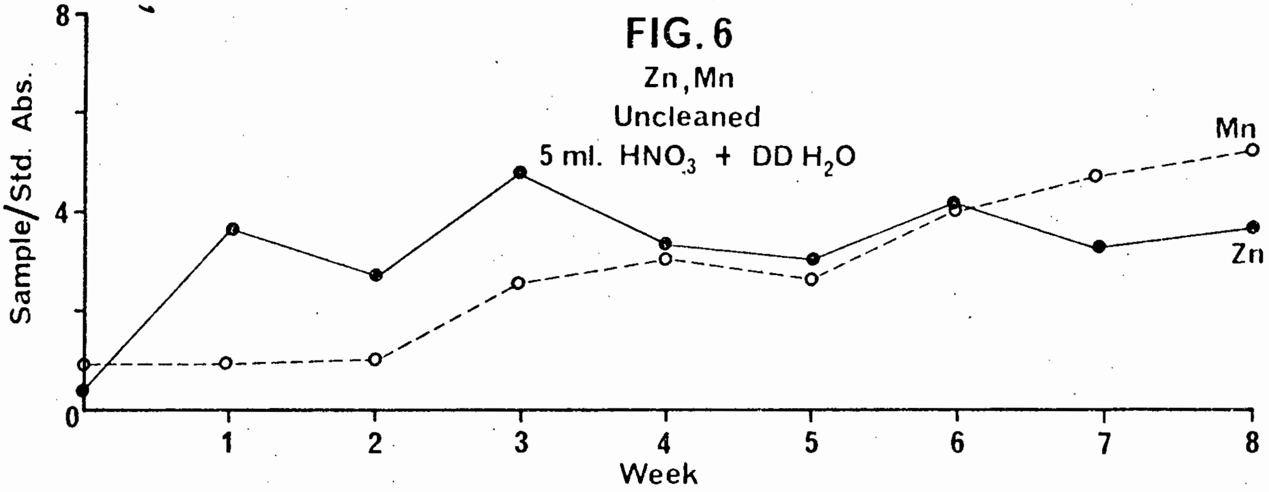


FIG. 6

Zn, Mn

Uncleaned

5 ml. HNO_3 + DD H_2O

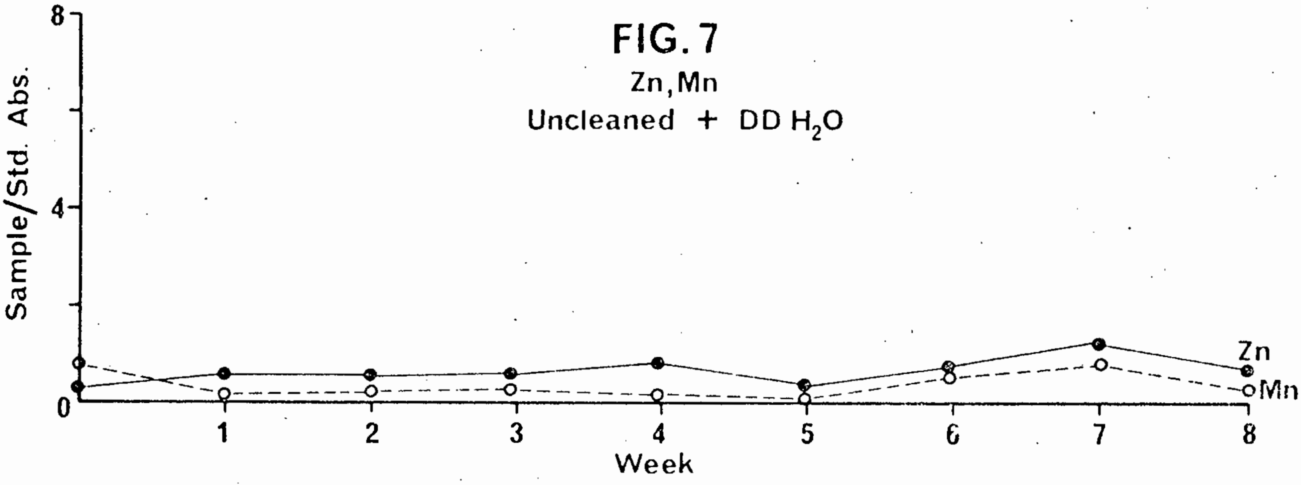


FIG. 7

Zn, Mn

Uncleaned + DD H_2O

FIG. 8

Co, Cu, Pb
HCl cleaned
5 ml. HCl + DD H_2O

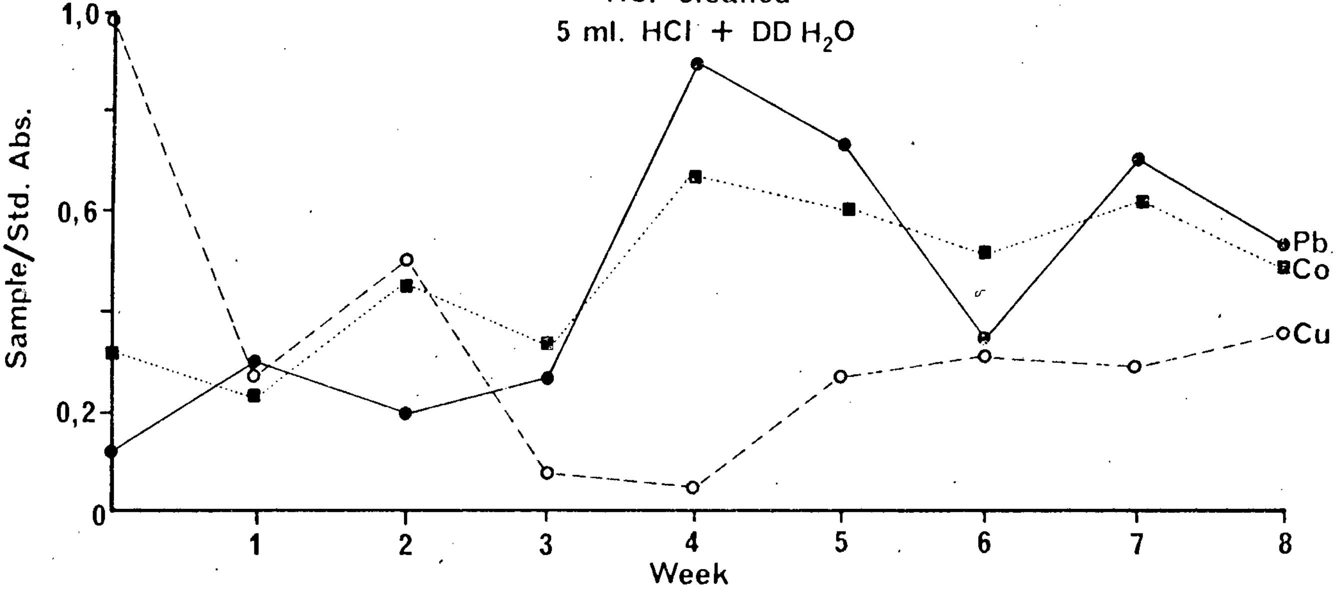


FIG. 9

Co, Cu, Pb
HCl cleaned + DD H_2O

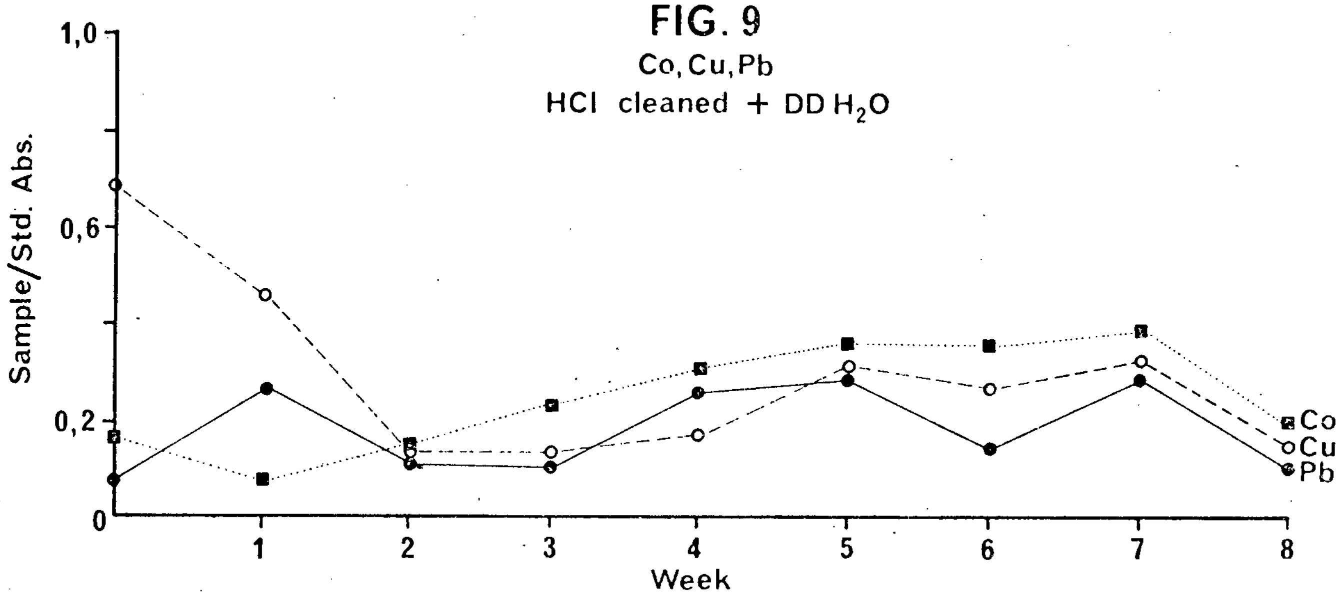


FIG.10

Cu,Co,Pb

HNO_3 cleaned

5 ml. HNO_3 + DD H_2O

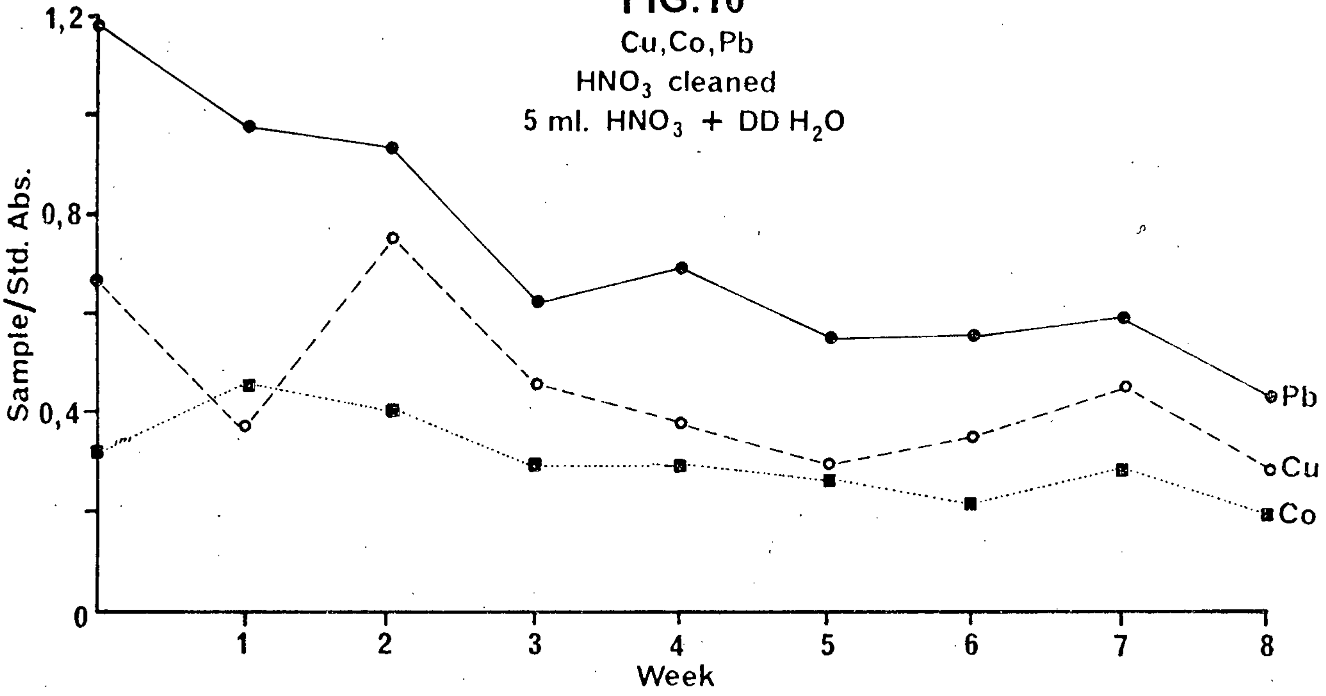


FIG.11

Cu,Co,Pb

HNO_3 cleaned + DD H_2O

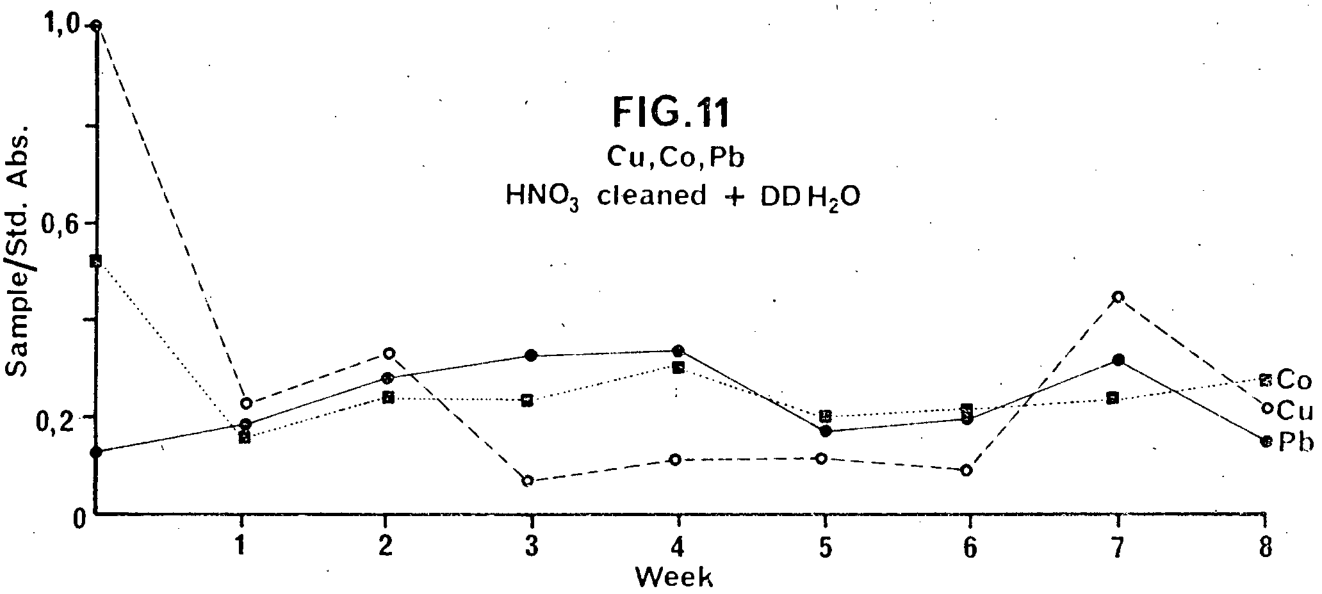


FIG. 12

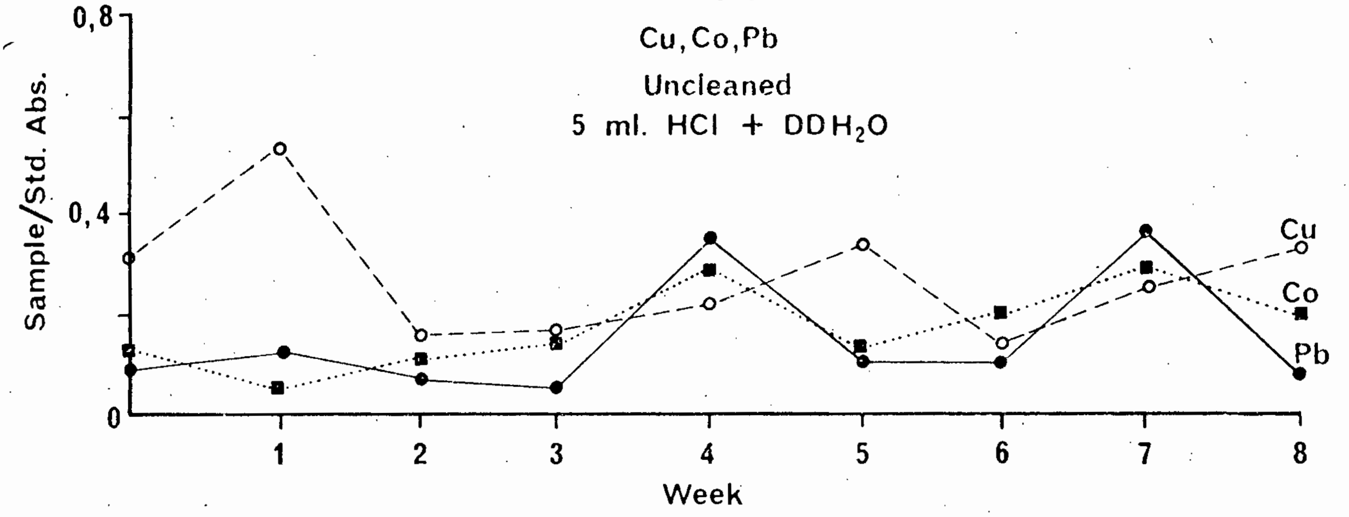


FIG. 13

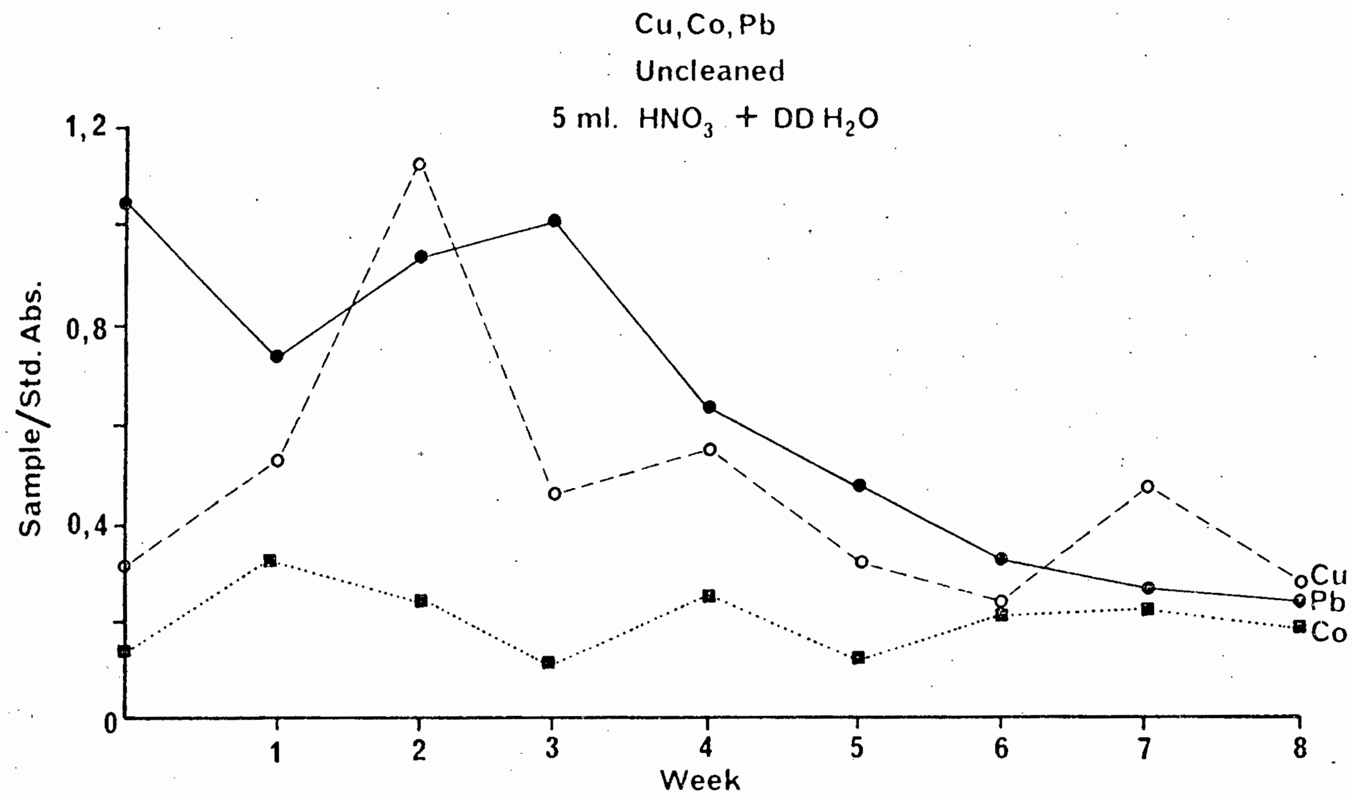


FIG. 14

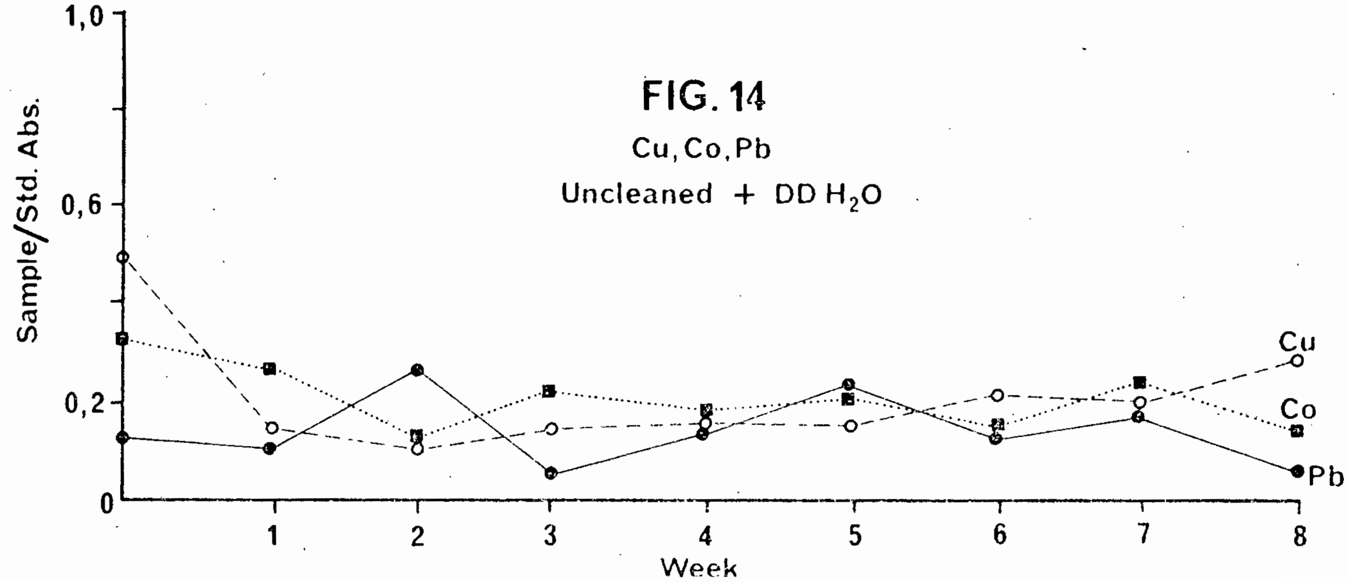


FIG. 15

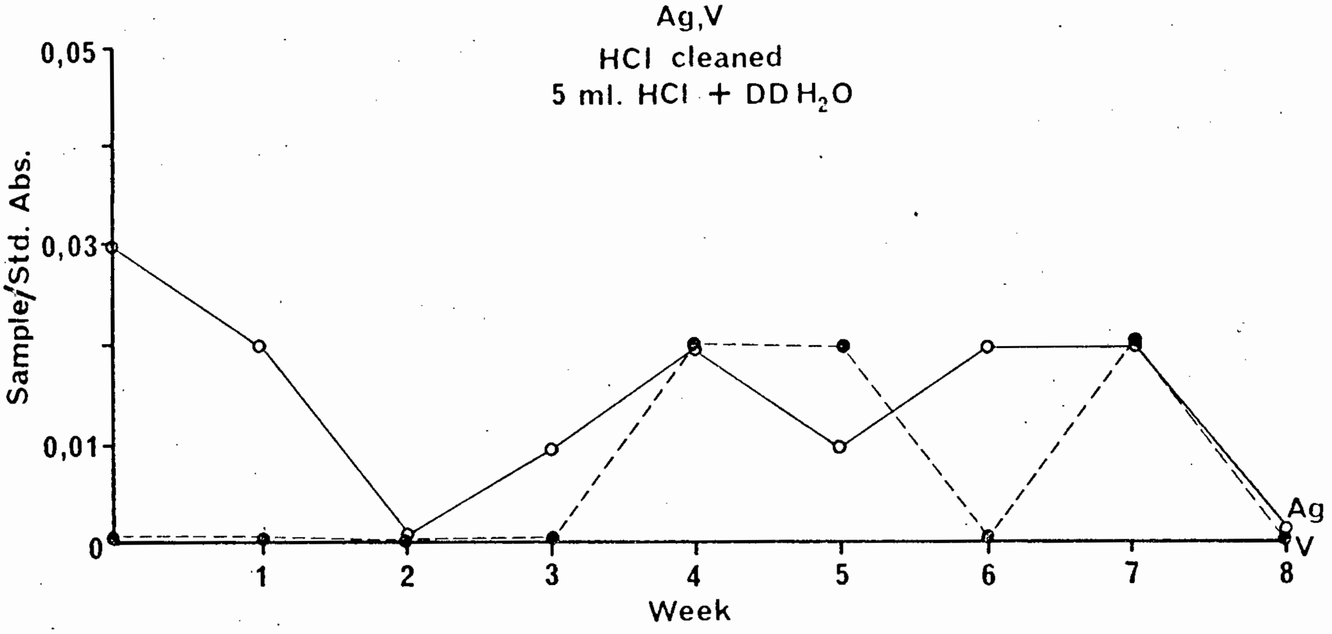

Ag,V
HCl cleaned
5 ml. HCl + DD H_2O
0,05
0,03
0,01
0
Sample/Std. Abs.
1
2
3
4
5
6
7
8
Week
Ag
V

FIG. 16

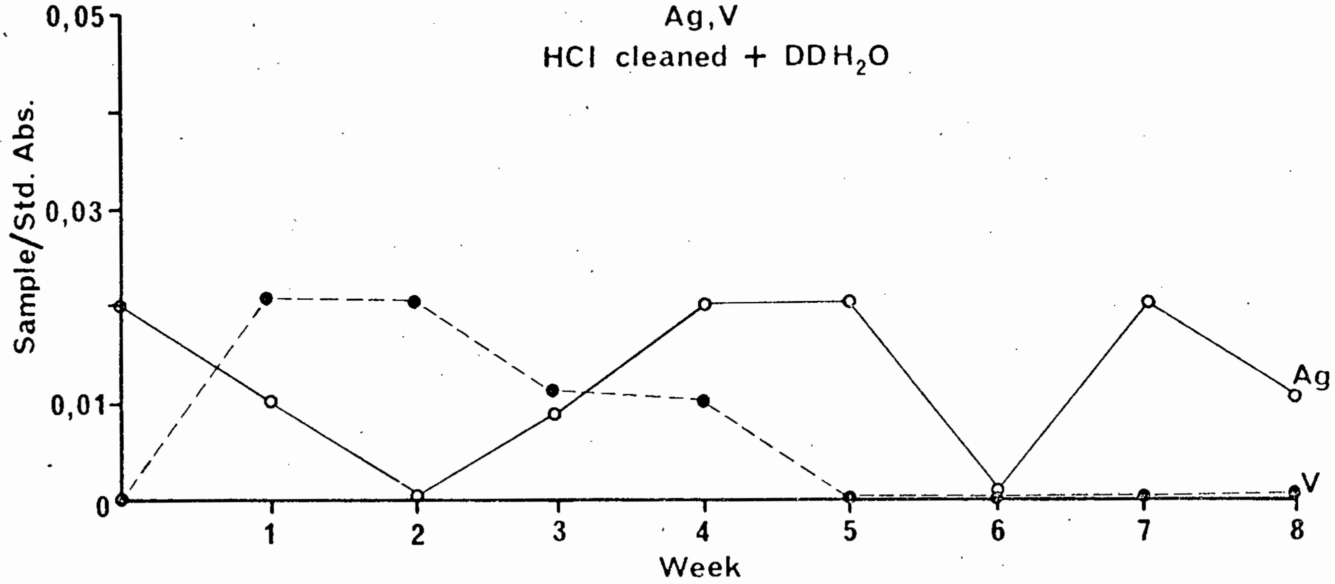

Ag,V
HCl cleaned + DD H_2O
0,05
0,03
0,01
0
Sample/Std. Abs.
1
2
3
4
5
6
7
8
Week
Ag
V

FIG. 17

Ag,V

HNO_3 cleaned

5 ml. HNO_3 + DD H_2O

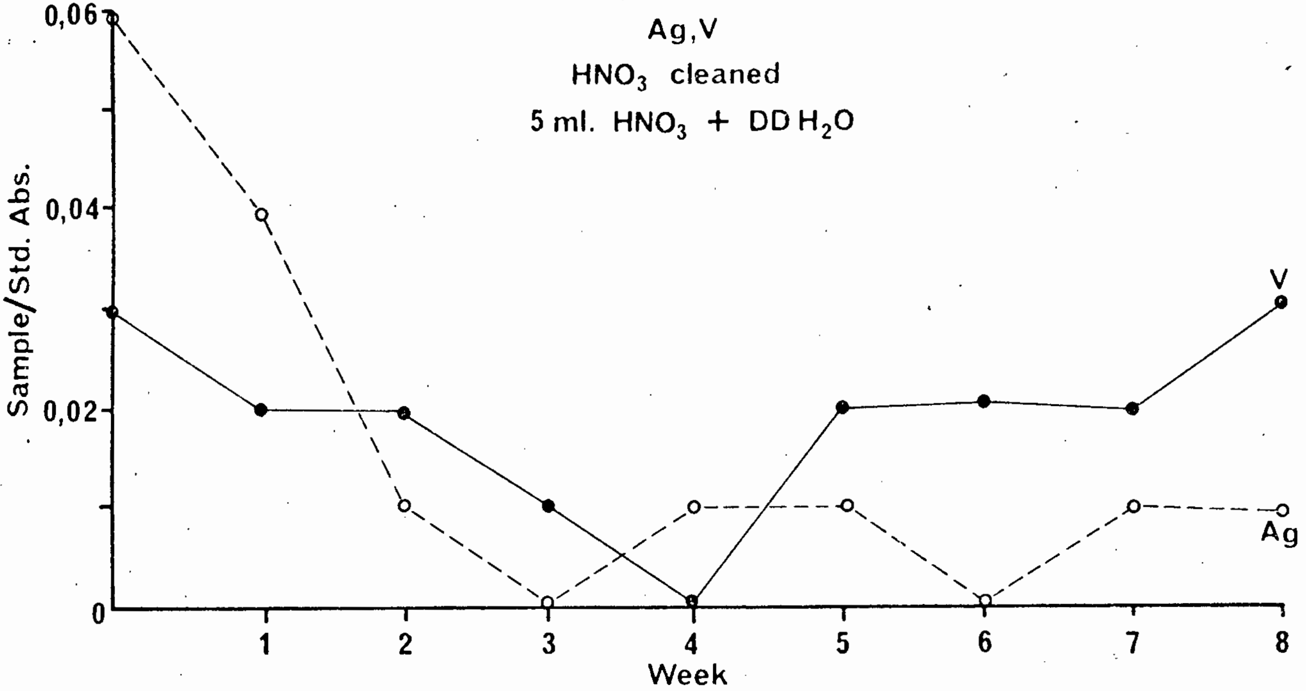


FIG. 18

Ag,V

HNO_3 cleaned + DD H_2O

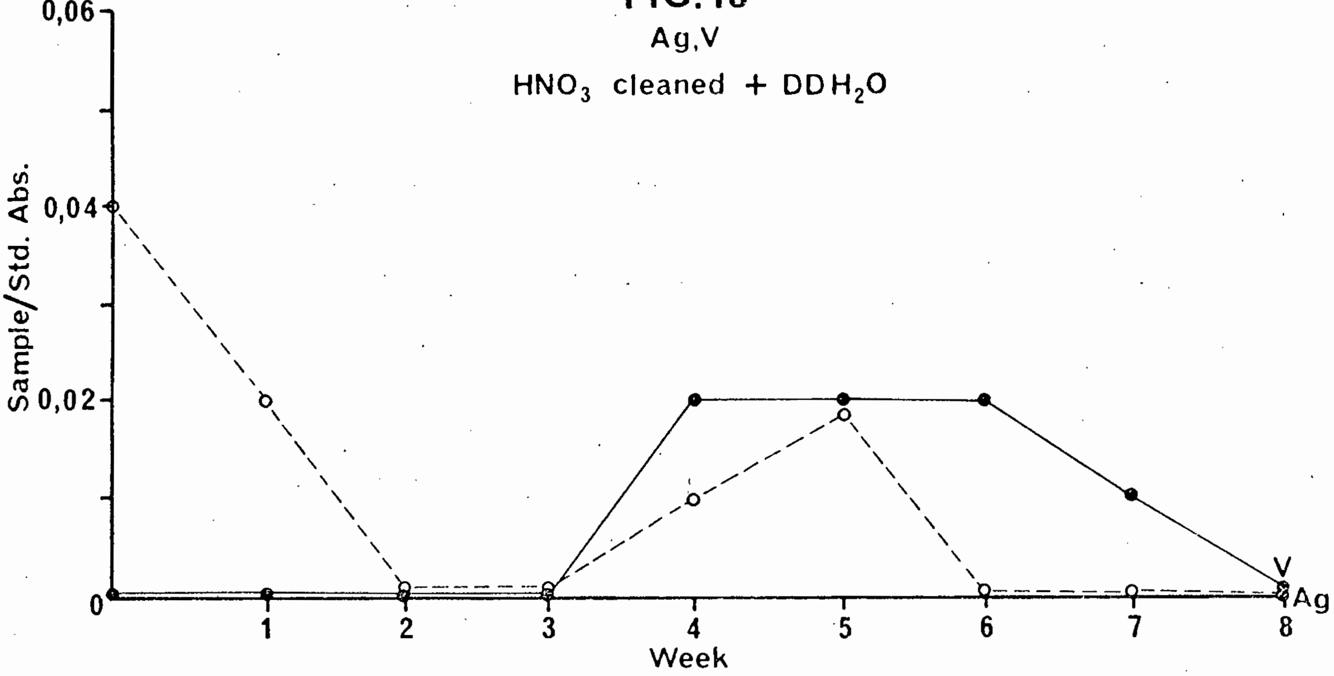


FIG. 19

Ag,V

Uncleaned

5 ml. HCl + DD H_2O

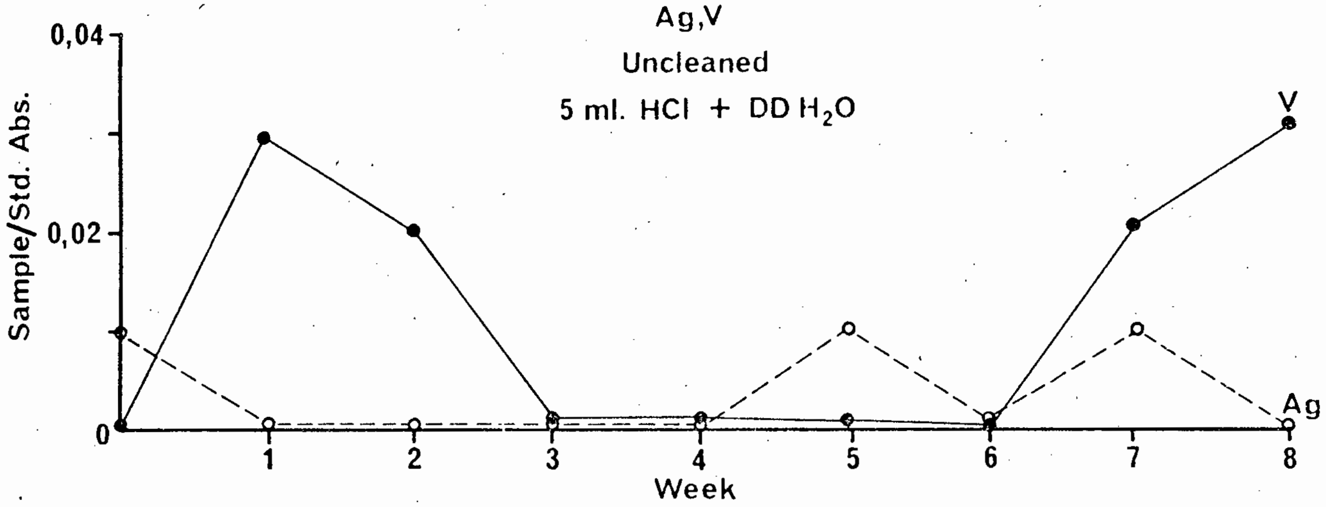


FIG. 20

Ag,V

Uncleaned

5 ml. HNO_3 + DD H_2O

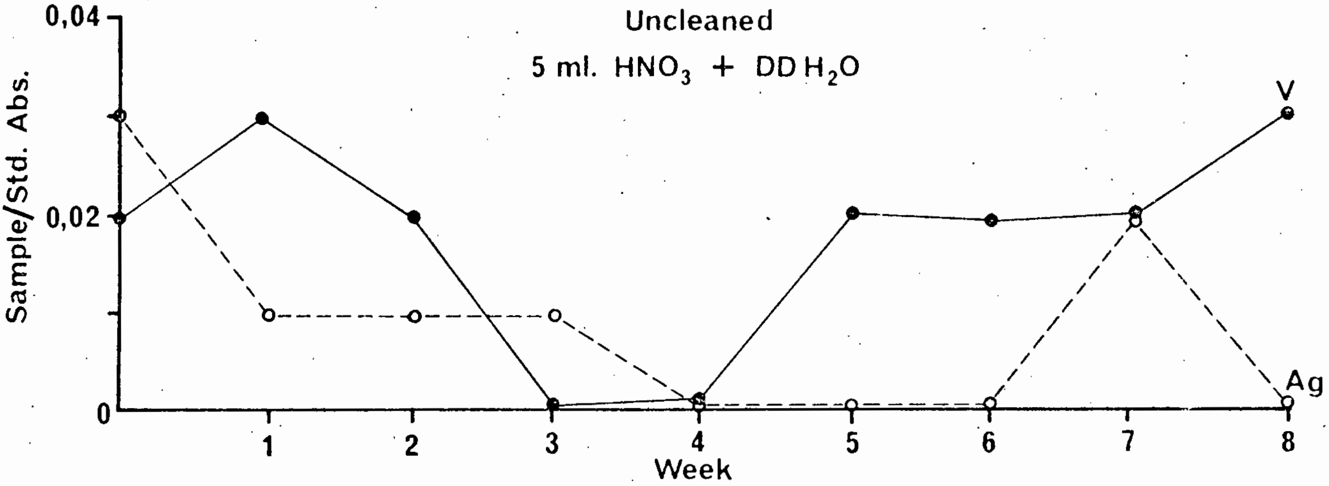


FIG. 21

Ag

Uncleaned + DD H_2O

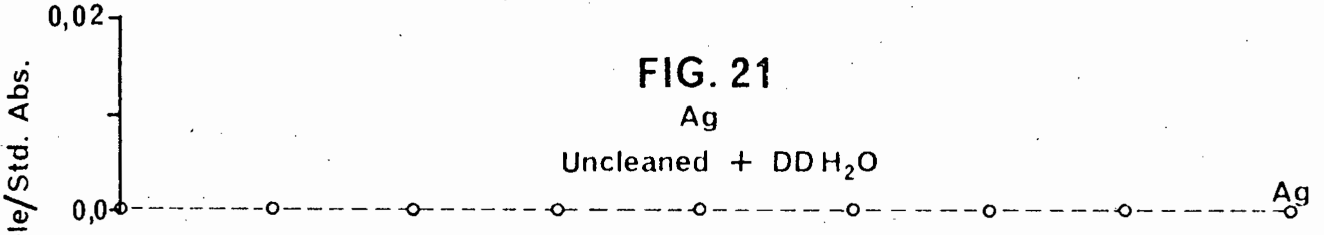


FIG. 22

V

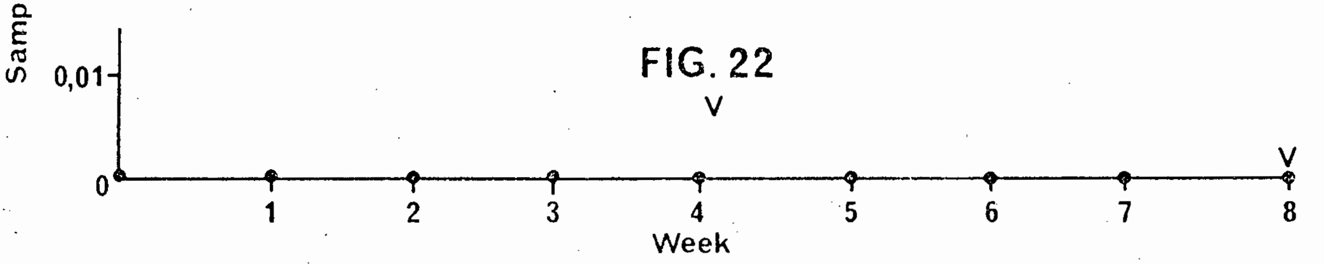


FIG. 23

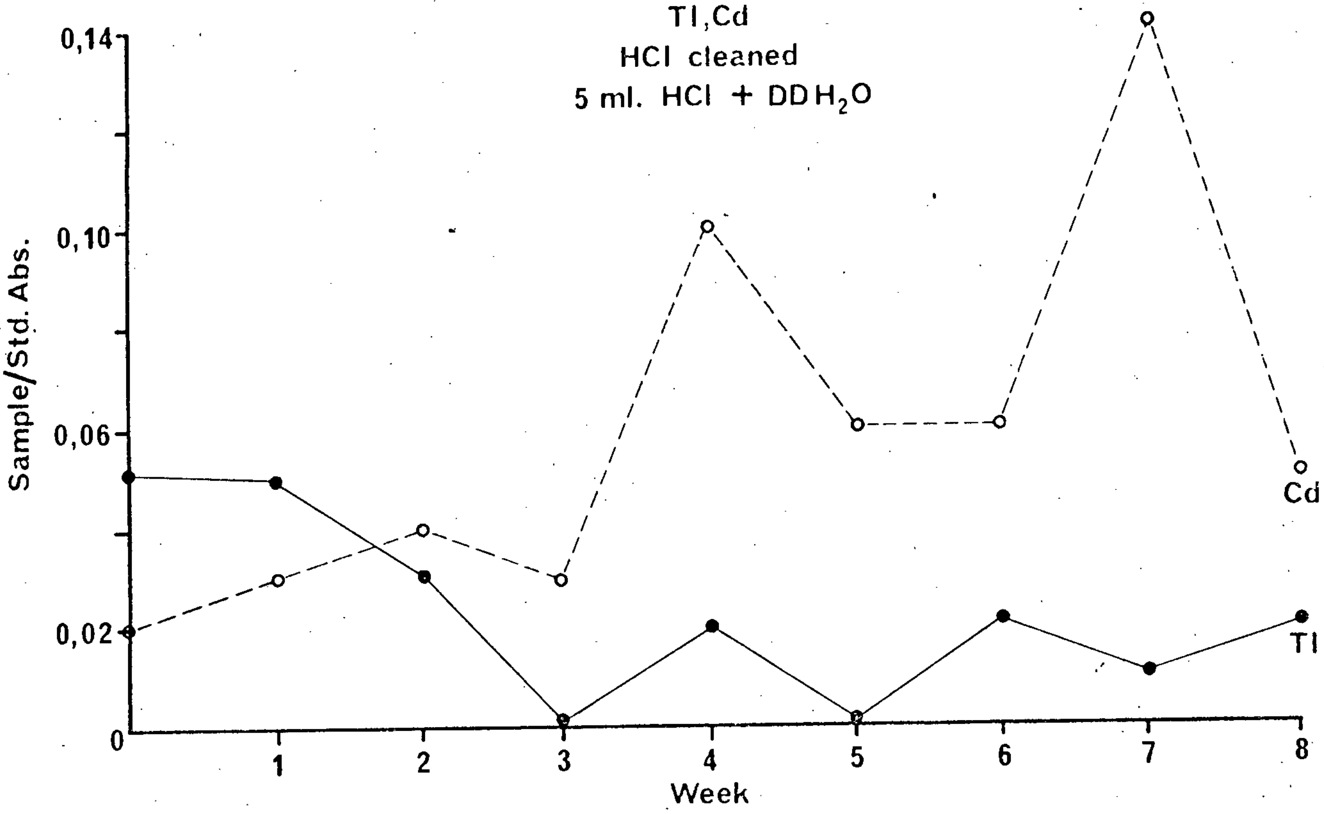

Tl,Cd
HCl cleaned
5 ml. HCl + DDH$_2$O
Sample/Std. Abs.
0,14
0,10
0,06
0,02
0
1
2
3
4
5
6
7
8
Week
Cd
Tl

FIG. 24

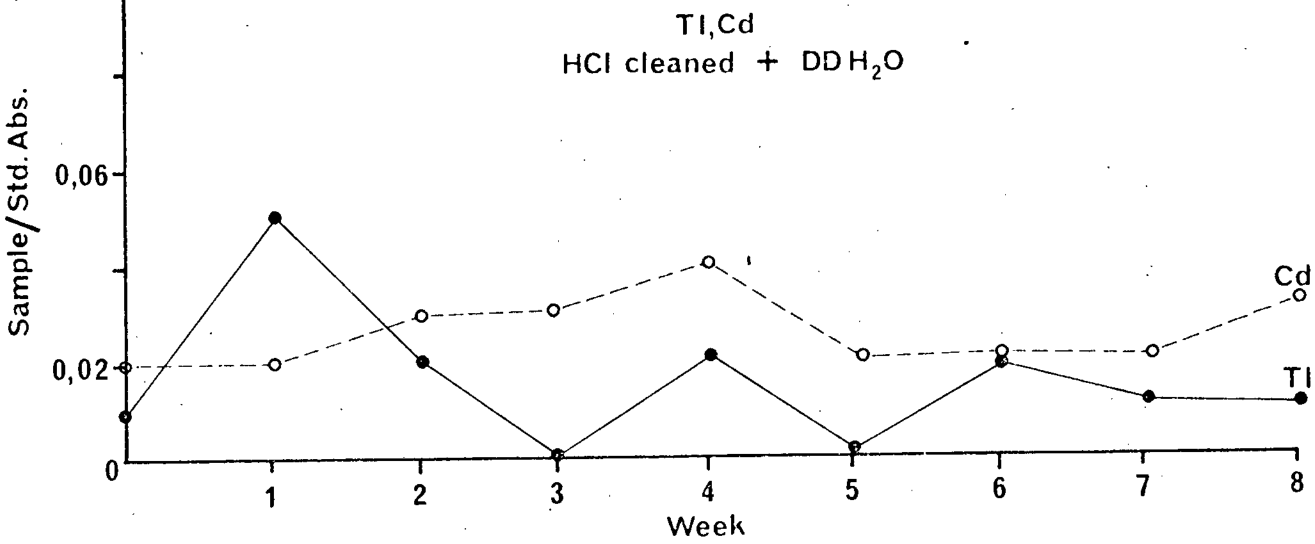

Tl,Cd
HCl cleaned + DDH$_2$O
Sample/Std. Abs.
0,10
0,06
0,02
0
1
2
3
4
5
6
7
8
Week
Cd
Tl

FIG. 25

Tl, Cd
HNO_3 cleaned
5 ml. HNO_3 + DDH_2O

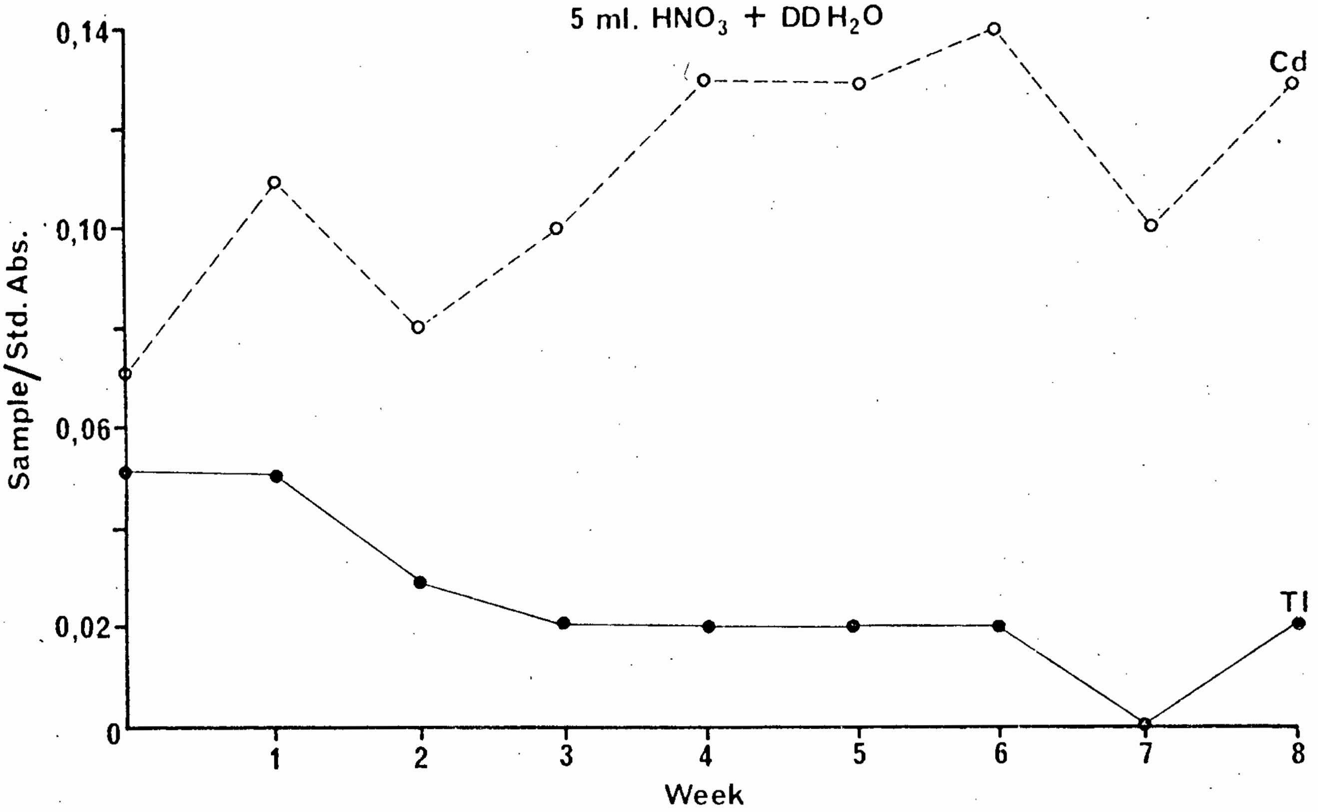
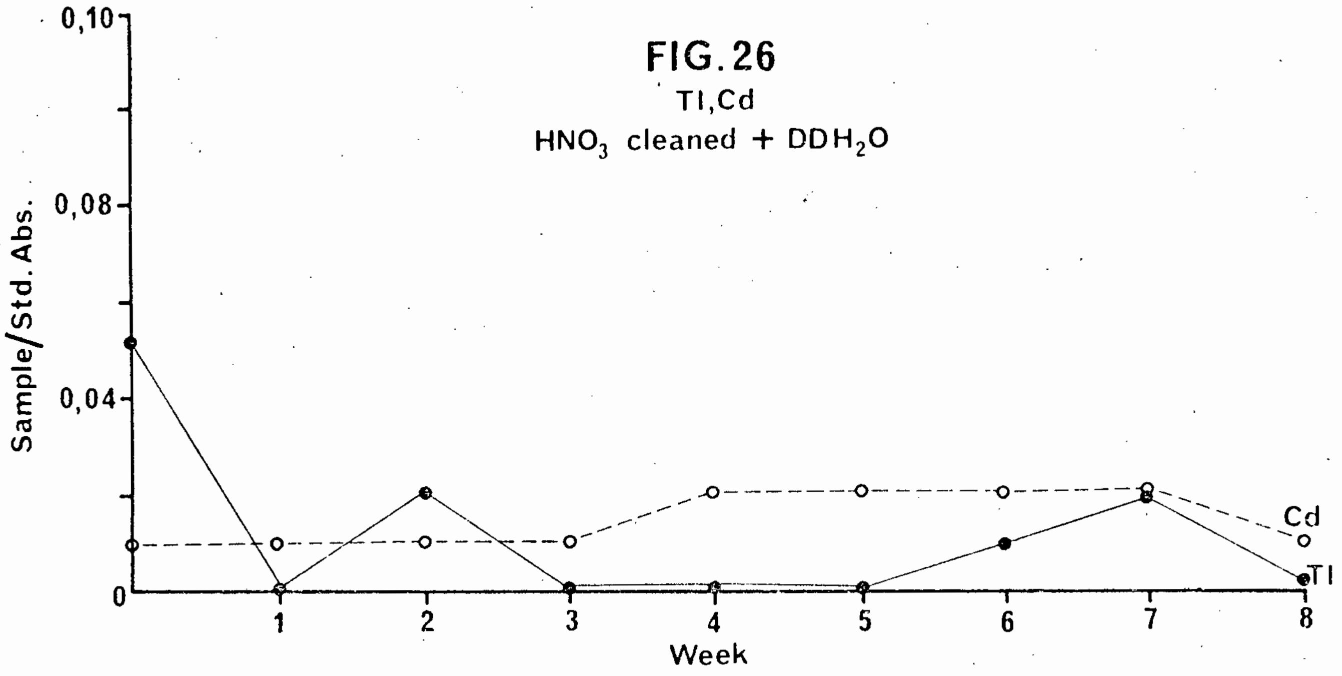


FIG. 26

Tl, Cd
HNO_3 cleaned + DDH_2O



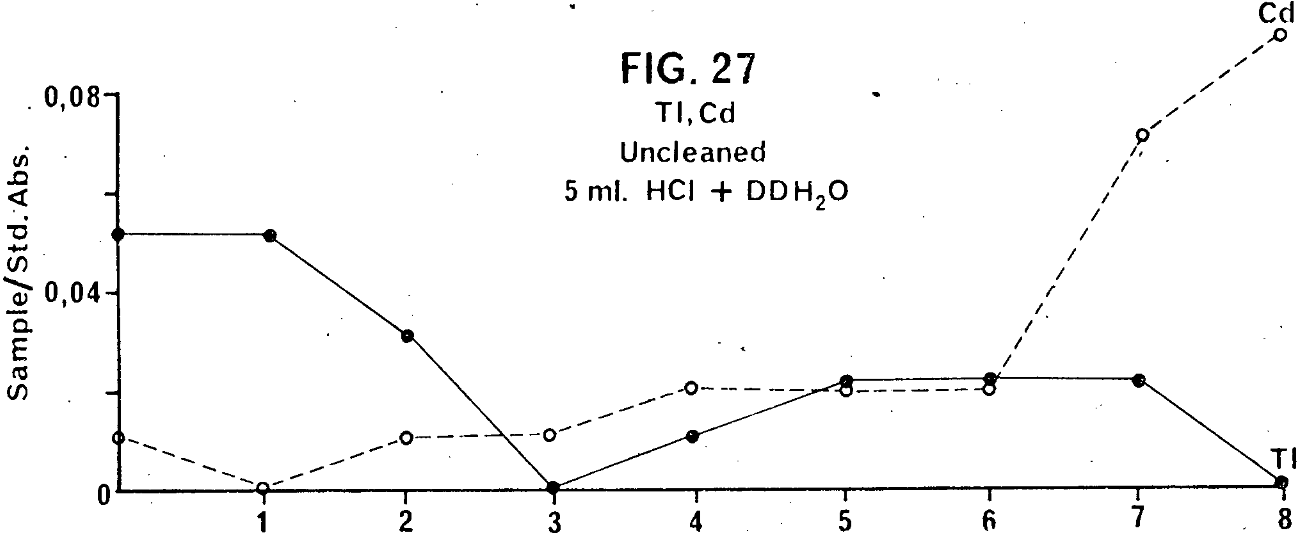


FIG. 27

Tl, Cd

Uncleaned

5 ml. HCl + DDH_2O

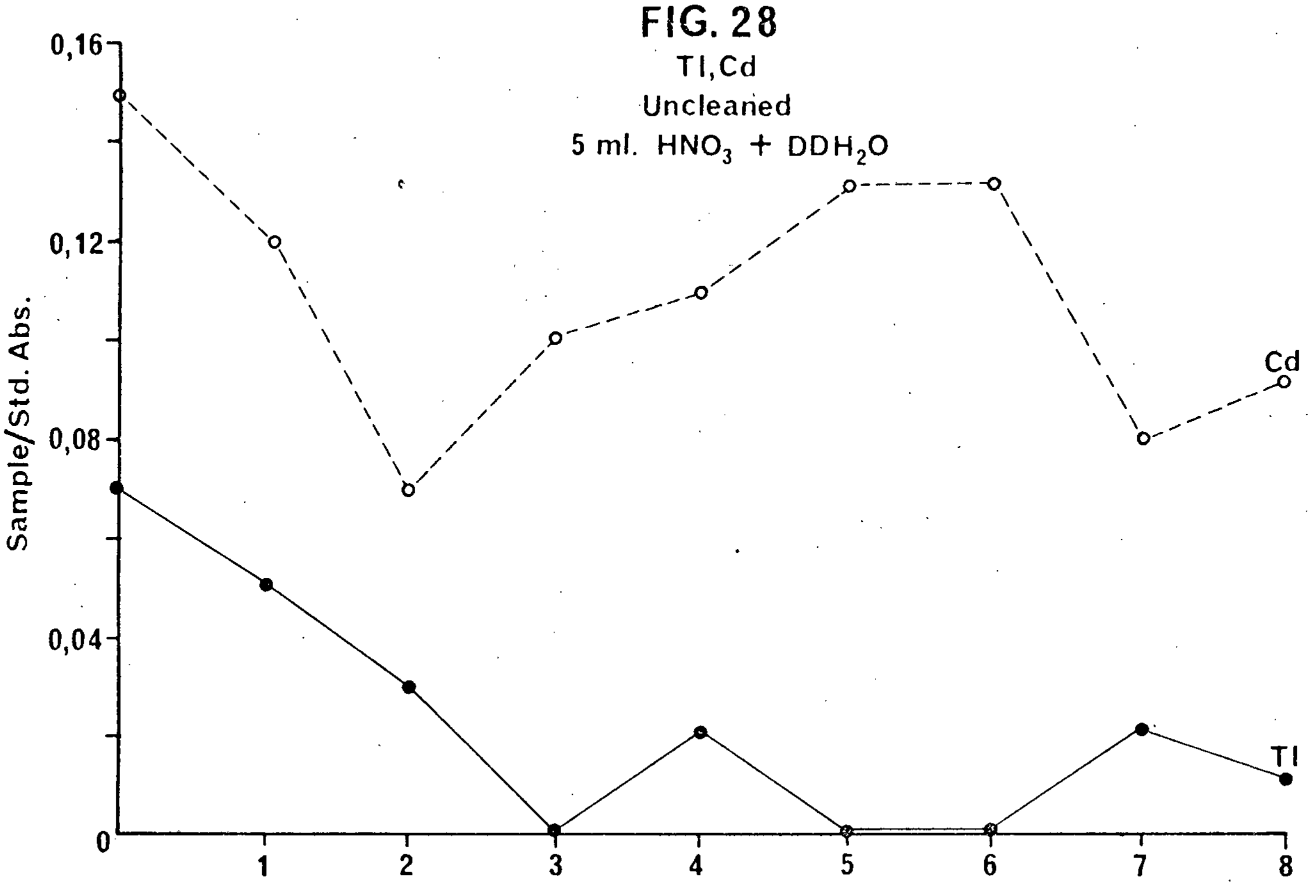


FIG. 28

Tl, Cd

Uncleaned

5 ml. HNO_3 + DDH_2O

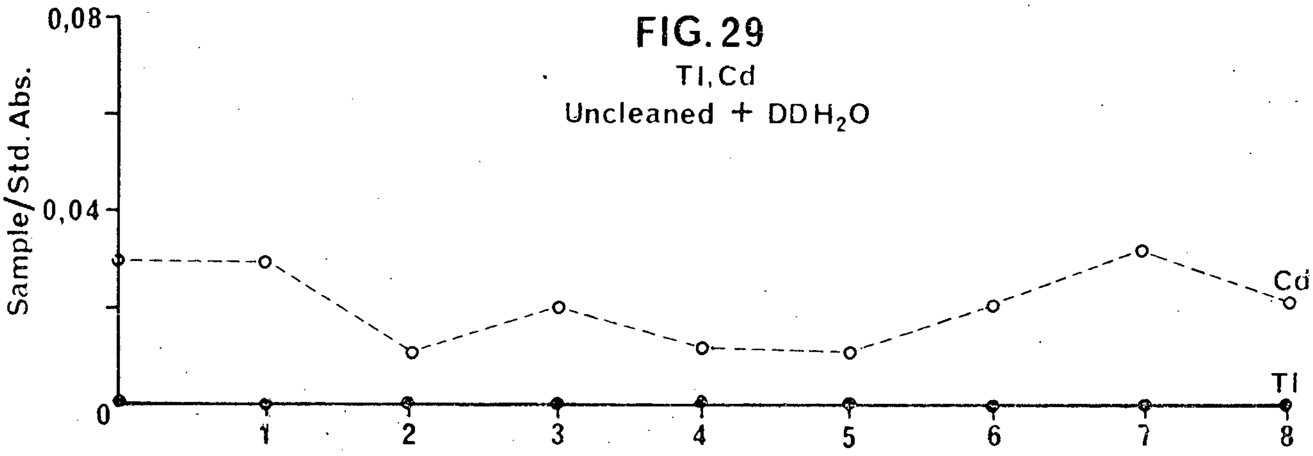


FIG. 29

Tl, Cd

Uncleaned + DDH_2O

the nominal concentrations are obtained by interpolation/extrapolation through one AAS standard value and the graphical origin of the absorbance/concentration plot. This nominal value will be reasonably accurate for sample/standard absorbance ratios near to 1, but become increasingly unreliable at higher values. The nominal concentrations should therefore be seen as no more than an approximate indication (order of magnitude) of the levels of concentration involved.

Before proceeding to a detailed examination of the data, it will be useful to examine some of the major implications of these results.

(i) As one might expect, the various solutions attack the containers to a lesser or greater degree, liberating different masses of specific elements in different samples (cf. for example , Figs.3, 4 and 7).

(ii) It appears that the <u>closure</u> (ie. the cap and its liner), and not the polyethylene bottle per se, is, in most cases at least, the principal victim of this attack. The fact that pre-cleaning polyethylene containers with acidic solutions reduces subsequent contamination of samples is very well established/18, 19, 20, 22, 29, 42, 43/. However, the data of Table 8 show clearly that at the end of the test period zinc contamination of the samples was, on average, much more severe in acid-cleaned containers than in those which were not cleaned.

Although it is accepted that the trace element content of various containers may be different (section 2.323), it seems improbable that this consistent relationship between cleaning and contamination in seven containers could be the result of chance. It is also improbable that the polyethylene was the major source of zinc, not only because this plastic is highly resistant to acids /60/, but also because it is relatively zinc-free compared to the closure (Table 3). The cardboard liner, on the other hand, had greater than 150 times more zinc per gram (equivalent to a maximum "mean" contamination of about 64 µg/l in an "average" water sample), and will be readily altered by acids. In many cases this alteration of the cardboard liner was clearly visible at the end of the test period.

The effect of the acidic attack becomes apparent if the containers are divided into groups related to the extent of exposure* to acid, as follows:

Group A: Non-corrosive environment - sample which was not acidified, and was stored in a container which was not pre-cleaned with acid.

Group B: Corrosive environment - samples which were acidified, but which were stored in containers that had not been cleaned with acid, OR, those which were not acidified, but which were stored in acid pre-cleaned containers.

Group C: Strongly corrosive environment - samples which were acidified and stored in acid pre-cleaned containers.

The Zn content of the sample in the water-rinsed bottle containing only double-distilled water (Group A) remained below 5 µg/1 (Appendix 2) throughout a total period of 12 weeks. It is suggested that the "non-corrosive", neutral pre-cleaning solution was unable to cause significant alteration of the closure, and subsequent contact between the neutral test sample and the closure therefore did not result in the leaching of significant amounts of Zn from this component.

In contrast to the above, notable changes in the Zn concentration occurred in the two pure water samples (Group B) which were stored in containers pre-cleaned with either HNO_3 or HCl. After 12 weeks the concentration of Zn in these samples was 31 and 37 µg/1 respectively. This suggests that pure water is able to leach significant amounts of Zn from closures altered by acidic pre-treatment.

Likewise, in the other two samples in Group B, the concentration of Zn recorded after 12 weeks in dilute HCl and HNO_3 were 59 and 48 µg/1 respectively. This further supports the suggestion that, unlike water alone, acidic samples are capable of leaching significant amounts of Zn from the closures - even if, as is the case

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* Recall that during pre-cleaning, the containers were filled with a 25% (v/v) acid solution and stored lying down for three weeks (Table 4).

here, there was no preliminary attack by a cleaning acid.

Predictably, zinc contamination was most severe in Group C. The two highest zinc concentrations recorded in this investigation were observed in the sample acidified with HNO_3 and stored in a container pre-cleaned with HNO_3 (79 μg/1), and in the corresponding sample where HCl was used for both pre-cleaning and acidification purposes (226 μg/1).

(iii) Table 3 shows that, in almost every case, the trace element content of the polyethylene is much lower than that of either the cap or the liner. The relative "flood" of contamination from the closure therefore makes is rather difficult to discern any effects which the polyethylene may have had on the sample solutions.

(iv) The deterioration of the cardboard liners also has a serious practical side-effect on the contamination experiment. Using zinc as an example, consider the following situation whithin a test container:

The principal source of zinc is the small, semi-porous, relatively extremely zinc-rich liner at the top of a full container which has virtually no air-space. The problem of obtaining a homogeneous distribution of microgram masses of zinc throughout the water sample under these circumstances is a severe one. When, in addition, microlitre quantities* of the sample are removed from the uppermost layers of the whole sample and analysed it becomes highly probable that the zinc content of this sub-sample may not be representative of the average for the whole 500 ml of solution. This problem becomes more extreme as the degree of inequilibrium between the zinc content of the bulk solution and the solution within the pore spaces of the altered liner rises.

It is suggested that the effects of this mixing problem can be seen in Figures 1 to 7 (Zn). Normally, under given circumstances, one expects better analytical precision at higher concentrations. However, the reverse holds here. In figure 7, (for the unattacked container, Group A), the zinc concentrations are low and uniform. In Figures 1 and 3 (for the most corroded containers, Group C), the zinc values are highest and very erratic. The Group B examples (Figures 2,4, 5 and 6) are roughly intermediate between these extremes.

Under these circumstances, one must be extremely circumspect about the interpretation of the week-to-week fluctuations shown in many of the figures 1 to 19. The manganese graphs in Figures 1 and 3 will serve to

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*This does not apply to the week 12 analyses which were by flame AAS.

illustrate the problem. Figure 3 shows a regular and unambiguous week-by-week increase in the concentration of Mn in a HNO_3 sample. In Figure 1 (Mn; HCl), on the other hand, the concentration of Mn fluctuates strongly, but it is impossible to claim that this is due to some property of the HCl in the absence of a guarantee that the two samples were both equally well mixed.

Bearing in mind the limitations imposed by the above points (i to iv), a more detailed examination of the data may now be made. For this purpose one may conveniently (although arbitrarily) group together those elements which behave similarly, as follows:

(a) In the case of Zn, Mn and Cd, the degree of contamination is, in some samples at least, quite obvious, and here it is possible to attempt some comparison of the effects of various cleaning and preservation procedures.

(b) For most of the other elements (except Pb), the contamination is, in most cases, so slight that the abovementioned comparison is probably not meaningful.

(c) Lead is a unique case; it is present in some types of acid in sufficiently high concentrations to cause blank problems which further complicate the interpretation of the data.

(a) ZINC, MANGANESE AND CADMIUM.

In all samples other than the one in Group A the zinc contamination is severe and far above the levels which would be acceptable in the Karroo project. HCl appears to leach Zn more readily than HNO_3. A comparison of Tables 3 and 8 suggests that by the twelfth week much of the zinc in the liners has been leached out, and that the bakelite cap may well have been slightly attacked too. However, Figure 7 suggests that the degree of zinc contamination might be drastically reduced if the sample solution was not allowed to contact the closure. Most of the above observations apply, mutatis mutandis, to manganese, but here the superiority of HCl as a leaching agent is less well defined. The results for Cd (Figures 23 to 29) again illustrate the mixing problem described earlier, but here the situation is exacerbated by the very small masses of Cd involved and the extreme sensitivity of the carbon rod AAS method to Cd.

Again, HCl seems to be a more powerful leaching agent than HNO_3. The latter acid has a higher Cd blank (cf. week 0 data).

Despite obvious differences between various samples, the absolute amount of Cd never rises above about 0,7 µg/1 (Fig. 23).

Therefore, in terms of the Karroo project, where concentrations of trace elements below 1 µg/1 would not normally be sought, the degree of Cd contamination from the Polykan containers would be negligible.

(b) THALLIUM, SILVER, COPPER, COBALT AND URANIUM.

The detection limit absorbance for the flameless AAS method was taken to be 0,004 under the conditons of this experiment. Since almost all of the absorbance measurements of Tl, Ag, Cu and Co in any samples were below 0,004, it follows that the absorbance ratios recorded for these elements in the Tables of Results are nominal and cannot be viewed as reflecting real week-to-week changes.

The approximate maximum levels of contamination reached for the various respective elements are : Tl 7 µg/1; Ag 0,1 µg/1; Cu 5 µg/1; and Co 3 µg/1. Since most of the observed values are well below these respective maxima, and since it is probable that these elements originate in the closures (Table 3), it is concluded that these elements will pose no serious contamination problems.

Uranium could not be detected (<about 1 µg/1) in any sample, and is therefore not a potential contaminant.

(c) LEAD.

The concentration of lead remained quite low in the "non-corrosive" Group A sample (Figure 14) and in most of the "corrosive" Group B samples (Figures 9, 11 and 12). There is some evidence of a systematic increase in the concentration of lead in the highly corrosive Group C - HCl sample (Figure 8), but the graph is rather erratic (probably because of poor mixing). The maximum lead concentration reached was less than 5 µg/1.

No comparison of the two acid types is possible, because Figures 10 and 13 show clearly that relatively large masses of lead (greater than 5 µ g/1) were introduced into the system at week 0 by the nitric acid. It is interesting to note that this lead disappears from solution quite systematically over the test period. It should also be noted that whereas Figure 8 shows erratic behaviour (leaching and non-mixing), Figures 10 and 13 are fairly regular, and correspond to samples where the Pb was well-mixed into the bulk solution in a single discrete aliquot.

The loss of Pb must have been due to adsorption onto the walls of the container. The total loss amounted to about 4 µg/l.

These observations lead to the very important conclusion that it is probably impossible to study "pure" contamination effects by ignoring adsorption phenomena. The one process must be seen as essentially the reverse of the other and even at extremely dilute concentrations a dynamic equilibrium will eventually be established which may, as in the above example, remove a metal from solution faster than it can be replaced.

2.334 CONCLUSIONS.

(i) The results of this experiment are in very good agreement with the predictions, implicit in the previous study (section 2.323), in which it was shown that (a) the principal contaminants were likely to be Zn and Mn (b) the other elements were unlikely to cause problems, and (c) the closure would be the principal source of contamination.

(ii) In any future experiments, steps should be taken to isolate the solutions from the closures so that the effect of the interaction between the sample and the polyethylene can be examined.

(iii) An experiment should be devised which will monitor the adsorption processes which may occur during, and thus complicate, contamination tests of this type.

(iv) Thereafter, an experiment should be set up to examine the overall real nett effect of simultaneous adsorption/contamination processes in dilute water samples.

2.34 A GAMMA-RAY SPECTROMETRIC STUDY OF THE TRACE ELEMENT ADSORPTION CHARACTERISTICS OF THE GIVEN TYPE OF POLYETHYLENE CONTAINER, USING RADIOACTIVE TRACER ISOTOPES FOR MONITORING CHANGES IN CONCENTRATION WITH TIME.

2.341 INTRODUCTION.

In accordance with the conclusions drawn in the preceding section (2.334), a radio-isotopic experiment was set up to examine some adsorption phenomena in the Polykan containers. Only the polyethylene was studied, and the closures were not involved at any stage. The selection of the elements studied was determined principally by the expense and availability of the isotopes required.

Extensive use has been made of radioactive isotopes as tracers in adsorption studies on various materials including glass, polyethylene and polypropylene /27, 28, 32a,b, 31, 35/. An advantage of this technique is that low concentrations of an element can be used if isotopes of high specific activity are available. Laboratory experiments of this nature can therefore be applied to those natural systems where concentrations of trace elements are typically within a similar range (ng to μg per litre levels). Another advantage is that contamination problems are minimal. Fourie /58/ has pointed out that the use of a radio-nuclide to predict the behaviour of the corresponding stable isotope in natural systems is only valid if the chemical forms of the two isotopes are similar. For example, it may prove difficult to use $Hg^{203}(NO_3)_2$ to study the rate of uptake of Hg by bacteria, if the bacteria are capable of assimilating Hg only in organo-mercurial forms.

It is assumed that the soluble radioactive tracers used in this experiment will behave similarly to their stable, soluble counterparts.

2. 342 EXPERIMENTAL METHOD.

(a) General.

Some previous workers (eg. /28/) have monitored the rate of adsorption of radioactive tracers by counting the activity of a sample of a given type of material after immersion in a tracer solution for a period of time. However, since autoradiography has shown that adsorption on some surfaces is inhomogeneous /32a/, this procedure was not favoured.

The method used here is essentially similar to that described by West *et al.* /32a/ and employed equipment and data reduction procedures which have been thoroughly documented by Fourie /58/. The rate of adsorption onto the polyethylene was monitored by measuring the activity of 5 ml aliquots removed from the bulk solution at intervals (zero, 1 day (most cases), 2,4,8, 16, 32 and 64 days). These aliquots were not returned to the bulk sample, but the nett effect of this small reduction in volume is negligible. A new vial was used to hold each new aliquot.

(b) Preparation of polyethylene containers.

A batch of 24 Polykan 57/500 containers was selected at random from the stock supply, and the cardboard sealing liners were removed from the caps. These bottles were divided into four groups which were treated as follows:

(1) Six bottles were pre-cleaned with 70% (v/v) nitric acid (Hopkin and Williams, Analar Grade) for 24 hours,

(2) Six bottles were pre-cleaned with 70% (v/v) hydrochloric acid (Merck 'Pro Analysi') for 24 hours,

(3) Six bottles were pre-cleaned with 70% (v/v) perchloric acid (May and Baker, Reagent Grade) for 24 hours, and

(4) Six bottles were pre-cleaned with double-distilled water for 24 hours.

After the pre-cleaning period, all bottles were emptied, and rinsed three times with double-distilled water.

(c) Preparation of sample solutions.

The isotopes selected had relatively long half-lives (Table 7) and intense gamma-ray emission. They were obtained from the Radiochemical Centre, Amersham, in the forms given in Table 7.

The concentrated radioisotopes were diluted to 25 ml with double-distilled water in all cases. It is not advisable to add relatively concentrated radioisotope spikes directly to a dry plastic container, since there is a danger of rapid surface adsorption (Meyer, pers. comm). Aliqots of the diluted isotope solutions were therefore added to containers partially filled with 200 ml of pure water and the theoretical amount of acid required to produce a final pH of 1,0. The containers were then topped up to 500 ml and the solutions were swirled carefully (avoiding contact with the bakelite cap) to ensure homogeneity.

Table 8 summarizes the preparation of the 12 duplicate samples in different acid media. The initial activities and corresponding approximate concentrations of these test samples are given in Table 9. They were stored upright at room temperature.

Table 7

Some properties of the radioisotopes used in this study.
(after Fourie /58/)

Isotope	Half-life (days)	Gamma-ray energy (keV)	Intensity γ/100 disintegrations	Counting time*(mins.)
Cr^{51}	27,7	320	9	10 (20)
Co^{58}	71,3	810	99	10 (100)
Fe^{59}	44,6	1 095	56	10 (100)
Zn^{65}	243,7	1 115	49	10 (100)

* Counting times for samples 1 to 8 are given in brackets.

Description of radioisotopes.

5 millicuries carrier-free Cr^{51} as chromic chloride in 0,1 M HCl, with a specific activity of 100 to 400 mCi/mg Cr;

5 millicuries carrier-free Co^{58} as cobaltous chloride in 0,1M HCl, with a specific activity of greater than 2 mCi/ug Co;

500 microcuries carrier-free Fe^{59} as ferric chloride in 0,1 M HCl, with a specific activity of 3 to 20 mCi/mg Fe; and

500 microcuries carrier-free Zn^{65} as zinc chloride in 0,1 M HCl, with a specific activity of greater than 100 mCi/mg Zn.

After preparation of the first eight samples, fresh and therefore more active solutions of Fe^{59} and Zn^{65} became available and were used:

5 millicuries carrier-free Fe^{59} as ferric chloride in 0,1 M HCl, with a specific activity of 3 to 20 mCi/mg Fe, and

2 millicuries carrier-free Zn^{65} as zinc chloride in 0,1 M HCl, with a specific activity of greater than 100 mCi/mg Zn.

(d) Measurement of activity.

The permanent fixed-geometry apparatus which was used is illustrated in Figure 30. A Ge(Li) semiconductor detector with an effective volume of 50 cm^3 and a resolution of 6 keV at 1 332 keV was used. It was cooled by liquid nitrogen in a large Dewar flask. This apparatus was shielded by a lead "castle". The associated multi-channel analyser had a memory of 1 024 channels.

The total number of counts per channel over the energy range of the measured radioisotope and the total counting time were typed by an on-line printer. The counting time for most samples (See Table 7) was such that at least 10 000 counts were accumulated, thereby giving theoretical statistical counting errors of less than 1%.

Instrumental drift (possibly caused by changes in humidity, temperature, etc.) was monitored by counting a Pb^{210} standard ($t\frac{1}{2}$ = 20,4 years) before and after each run. Variations in the count rate of this standard before and after each run were less than 1% (at about 5 000 counts/min.), while the variation between the maximum and minimum count rates observed throughout the whole 64 day test period was 2,31%.

No absolute calibration of the system was neccessary, since the measured activities, after being corrected for natural decay, were always compared to the day zero activity in order to monitor relative changes.

The number of observations made was practically limited by the fact that the data had to be reduced partially by hand.

Table 8

Preparation of the 12 duplicate sets of samples in different acid media.

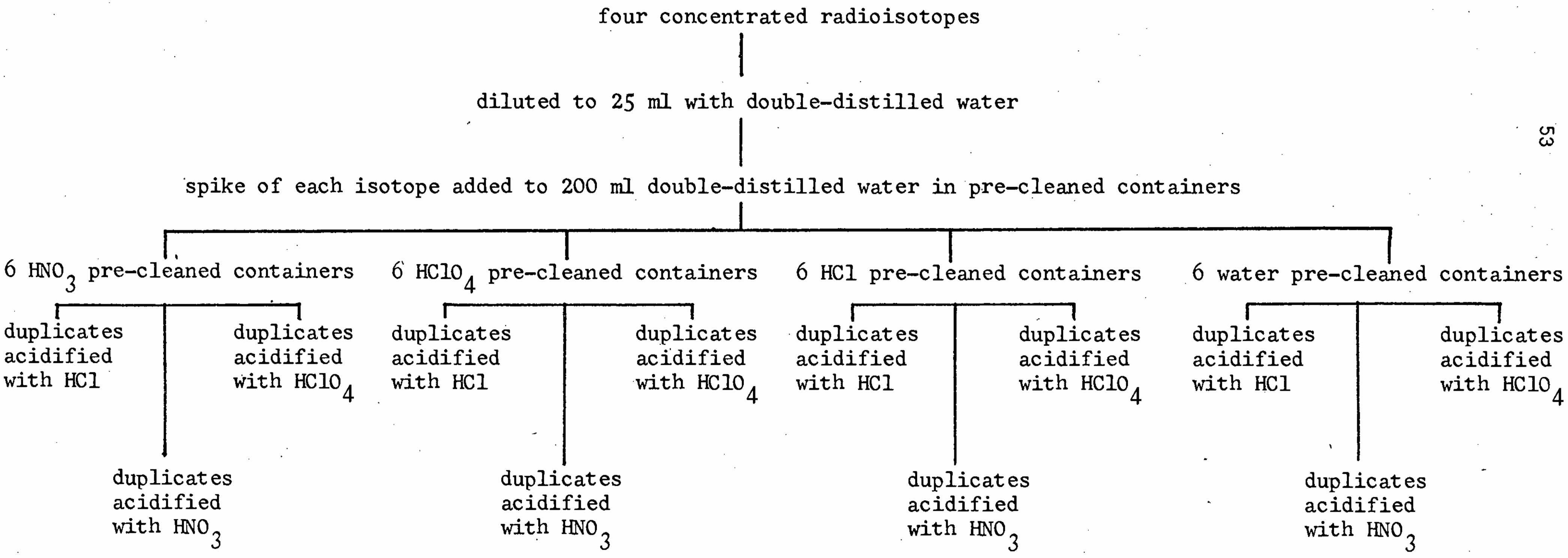

Table 9

Initial activities* and approximate concentrations** of the test samples.

Sample No.	Cr^{51}	Co^{58}	Fe^{59}	Zn^{65}
1 and 3	40 µCi (0,74)	40 µCi (<0,032)	20 µCi (3,4)	20 µCi (0,15)
2 and 4 to 8	80 µCi (1,48)	40 µCi (<0,032)	20 µCi (3,4)	20 µCi(0,15)
9 to 23 (except 13)	240 µCi (4,44)	240 µCi (<0,192)	300 µCi (63,4)	120 µCi (1,0)
13	240 µCi (4,44)	240 µCi (<0,192)	600 µCi (126,8)	120 µCi (1,0)
24	240 µCi (4,44)	240 µCi (<0,192)	150 µCi (31,7)	120 µCi (1,0)

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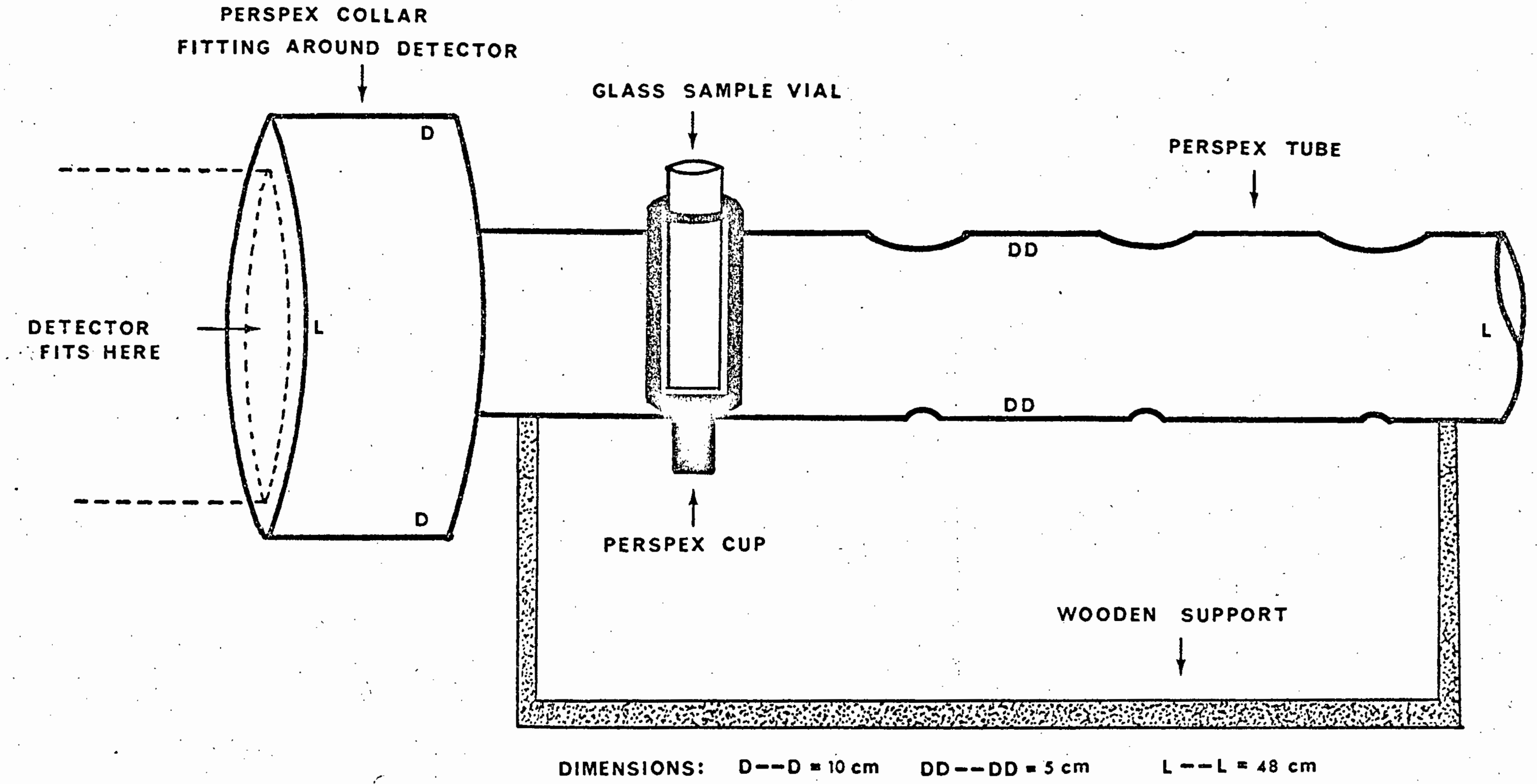
* in a sample volume of 500 ml

** concentrations (in brackets) in each case are in µg/l.

Figure 30

Fixed-geometry sample holder for measurement of activity.



2.343 RESULTS.

2.3431 CALCULATIONS AND STATISTICAL ANALYSIS.

In theory, the form of a peak of mean energy E in the energy spectrum can be represented by a Gaussian distribution, but in practice this curve is slightly skewed towards the low-energy side of the peak. The gross number of counts observed over the energy range covered by such a peak consist of the gamma-ray emmission from the sample, together with background counts from other sources such as natural radioactivity and cosmic rays.

To eliminate the background, it is assumed that the energy spectrum on either side of the peak forms part of the background continuum, which does not change significantly under the peak. Thus the nett peak is simply the difference between the integrated peak and integrated background values measured to either side.

Calculation of the standard deviation (σ) is the most common method of statistical analysis of counting errors. Since the decay of an isotope is in itself a statistical process due to the large number of occurrences taking place, it can be assumed that the measured standard deviation is the same as the theoretical standard deviation for an infinite number of events. Under these circumstances the standard deviation is given by the square root of the number of events. The number of counts is therefore reported as

$$n \pm \sqrt{n} = n \pm \sigma$$

Since both the peak (n_p) and background (n_b) counts involve this uncertainty, the nett peak count is represented as

$$n_p - n_b \pm \sqrt{(\sigma_p)^2 + (\sigma_b)^2}$$

The nett integrated peak counts were normalized for natural decay according to the standard decay law

$$N = N_o e^{-\lambda t}$$

where N is the activity at time t,

N_o is the activity at t=0,

λ is the decay constant for the isotope,

and t is the time elapsed.

When the half-life of the radioisotope is long compared to the time

Table 10

Percentage changes in original solution activity of Cr^{51} with time.

Duplicate number	Percentage change after						
	1 day	2 days	4 days	8 days	16 days	32 days	64 days
1		-4,12 ± 2,28	-1,24 ± 2,25	-1,33 ± 2,23	-5,65 ± 2,18	+0,79 ± 2,09	-6,59 ± 1,96
		+1,65 ± 1,33	-1,22 ± 1,32	+1,14 ± 1,30	-5,01 ± 1,25	-3,49 ± 1,19	-2,63 ± 1,11
2		-1,39 ± 2,27	+0,14 ± 2,27	-0,43 ± 2,22	+2,45 ± 2,17	-4,16 ± 2,07	-5,03 ± 1,93
		-1,89 ± 1,35	+1,31 ± 1,34	+1,56 ± 1,33	+2,17 ± 1,28	+1,90 ± 1,22	-0,21 ± 1,13
3		+4,65 ± 1,40	+5,22 ± 1,39	-5,41 ± 1,34	+5,67 ± 1,32	+2,40 ± 1,25	+7,03 ± 1,16
		-0,18 ± 1,39	+1,27 ± 1,38	+0,86 ± 1,36	-0,08 ± 1,31	+0,56 ± 1,25	-6,53 ± 1,16
4		+0,78 ± 1,39	+1,56 ± 1,38	-0,45 ± 1,36	+1,43 ± 1,32	+1,37 ± 1,25	-0,74 ± 1,16
		-1,79 ± 1,37	-2,86 ± 1,35	-4,37 ± 1,32	-5,63 ± 1,28	-3,04 ± 1,22	-8,81 ± 1,14
5	-6,74 ± 2,19	-0,38 ± 2,20	-1,20 ± 2,18	-1,70 ± 2,14	-0,99 ± 2,11	+0,32 ± 2,00	+8,78 ± 1,87
	-2,82 ± 2,27	+1,34 ± 2,29	+0,77 ± 2,27	+3,01 ± 2,23	-0,63 ± 2,18	+5,11 ± 2,09	-2,70 ± 1,95
6	+0,14 ± 2,31	-1,06 ± 2,27	+0,71 ± 2,25	-1,25 ± 2,21	-4,91 ± 2,16	+2,65 ± 2,07	-4,00 ± 1,93
	-3,53 ± 2,25	-1,52 ± 2,26	-0,93 ± 2,24	+4,03 ± 2,21	-0,34 ± 2,15	+2,83 ± 2,06	+5,25 ± 1,92
7	-1,63 ± 2,67	+5,99 ± 2,67	+4,42 ± 2,65	-2,03 ± 2,61	-1,73 ± 2,54	+3,65 ± 2,43	+4,16 ± 2,26
	+0,72 ± 2,31	+3,21 ± 2,32	+4,14 ± 2,29	-2,05 ± 2,26	+4,39 ± 2,21	+5,71 ± 2,11	+7,54 ± 1,97
8	-0,24 ± 2,34	+2,56 ± 2,33	+3,76 ± 2,32	+4,31 ± 2,29	+2,86 ± 2,24	+7,06 ± 2,14	+7,13 ± 2,00
	-3,24 ± 2,23	+0,04 ± 2,22	-3,55 ± 2,21	-1,08 ± 2,18	-3,07 ± 2,13	+3,63 ± 2,03	+2,39 ± 1,89
9	-2,82 ± 2,30	+1,81 ± 2,30	-3,37 ± 2,29	+6,48 ± 2,26	-2,76 ± 2,21	+7,77 ± 2,11	+7,57 ± 1,97
	-2,10 ± 2,25	-2,68 ± 2,25	-2,79 ± 2,24	-4,96 ± 2,21	+0,90 ± 2,15	+3,88 ± 2,06	+5,00 ± 2,00
10	+0,51 ± 2,30	+2,46 ± 2,30	+4,41 ± 2,29	+1,40 ± 2,26	+1,91 ± 2,21	-4,02 ± 2,11	+3,98 ± 1,97
	+6,05 ± 2,37	+4,28 ± 2,37	-1,32 ± 2,35	+4,99 ± 2,34	+8,80 ± 2,30	+6,19 ± 2,27	+2,60 ± 2,20
11	-5,58 ± 2,22	+0,73 ± 2,22	-0,49 ± 2,20	-4,16 ± 2,20	+1,08 ± 2,15	-4,09 ± 2,10	-5,91 ± 2,05
	+0,45 ± 2,22	+0,22 ± 2,22	-0,50 ± 2,20	-1,24 ± 2,20	-1,12 ± 2,15	-3,78 ± 2,10	+6,18 ± 2,05
12	-0,09 ± 2,30	-1,94 ± 2,30	+4,35 ± 2,28	-0,60 ± 2,25	-1,39 ± 2,20	+0,41 ± 2,17	+1,65 ± 2,10
	-0,66 ± 2,10	+1,94 ± 2,10	+2,19 ± 2,07	+1,80 ± 2,07	+1,22 ± 2,05	-0,52 ± 2,00	-4,43 ± 1,95

Table 11

Percentage changes in original solution activity of Co^{58} with time.

Duplicate number	Percentage change after						
	1 day	2 days	4 days	8 days	16 days	32 days	64 days
1		-2,09 ± 0,29	-1,53 ± 0,29	-2,12 ± 0,29	-1,96 ± 0,28	-2,12 ± 0,27	-4,13 ± 0,26
		-0,19 ± 0,29	-1,51 ± 0,29	-2,83 ± 0,28	-3,80 ± 0,28	-1,53 ± 0,27	-2,65 ± 0,26
2		+4,02 ± 0,31	+3,73 ± 0,31	+0,72 ± 0,30	+3,28 ± 0,30	+3,86 ± 0,29	+3,65 ± 0,27
		+2,13 ± 0,30	+3,34 ± 0,30	+4,38 ± 0,30	+2,77 ± 0,29	+2,53 ± 0,28	+2,80 ± 0,27
3		+3,91 ± 0,30	+4,32 ± 0,30	-4,89 ± 0,29	+2,65 ± 0,29	+2,84 ± 0,28	+2,77 ± 0,27
		+1,14 ± 0,30	+1,06 ± 0,30	+0,03 ± 0,30	-1,05 ± 0,29	-1,42 ± 0,28	+0,13 ± 0,27
4		+2,08 ± 0,31	-1,36 ± 0,30	-0,92 ± 0,30	-1,55 ± 0,29	-1,16 ± 0,28	-1,03 ± 0,27
		+0,10 ± 0,31	-0,18 ± 0,30	-0,36 ± 0,30	-3,69 ± 0,29	+0,12 ± 0,29	-1,65 ± 0,27
5	-0,58 ± 0,48	+1,66 ± 0,48	+1,73 ± 0,47	-0,56 ± 0,47	+0,69 ± 0,46	+3,04 ± 0,45	+2,18 ± 0,42
	-3,83 ± 0,48	+1,21 ± 0,49	+0,68 ± 0,49	-0,67 ± 0,48	+0,92 ± 0,47	+1,58 ± 0,46	+2,16 ± 0,43
6	+7,73 ± 0,52	+9,29 ± 0,52	+9,03 ± 0,52	+9,98 ± 0,51	+8,55 ± 0,50	+9,25 ± 0,49	+8,94 ± 0,45
	-4,01 ± 0,47	-0,90 ± 0,47	-2,12 ± 0,47	-1,16 ± 0,47	-0,82 ± 0,46	-0,86 ± 0,44	+1,10 ± 0,42
7	-2,73 ± 0,52	-0,71 ± 0,52	-1,16 ± 0,52	+0,24 ± 0,51	-1,62 ± 0,50	+0,96 ± 0,48	+1,78 ± 0,45
	-1,00 ± 0,48	+0,06 ± 0,48	+0,34 ± 0,47	-0,14 ± 0,47	-0,03 ± 0,46	+0,46 ± 0,44	+0,96 ± 0,42
8	+0,93 ± 0,48	+0,49 ± 0,48	+1,97 ± 0,47	+2,88 ± 0,47	+2,54 ± 0,46	+1,61 ± 0,44	+2,97 ± 0,45
	+0,04 ± 0,47	-0,07 ± 0,47	+0,57 ± 0,46	-0,20 ± 0,46	-0,07 ± 0,45	+1,52 ± 0,43	+0,20 ± 0,41
9	+0,81 ± 0,50	+4,38 ± 0,50	+3,56 ± 0,49	+3,59 ± 0,49	+4,73 ± 0,47	+4,63 ± 0,46	+3,97 ± 0,45
	-1,29 ± 0,47	-2,74 ± 0,47	-2,52 ± 0,47	-2,61 ± 0,46	-0,24 ± 0,45	-0,24 ± 0,45	-0,68 ± 0,44
10	-1,57 ± 0,48	-0,77 ± 0,48	-1,09 ± 0,47	-1,90 ± 0,46	+0,16 ± 0,45	+1,16 ± 0,44	+0,01 ± 0,42
	+0,51 ± 0,48	+2,19 ± 0,48	+2,30 ± 0,48	+0,59 ± 0,47	+2,90 ± 0,45	+1,90 ± 0,43	+2,46 ± 0,40
11	-1,50 ± 0,47	-0,15 ± 0,47	+1,00 ± 0,46	-1,76 ± 0,45	+0,58 ± 0,44	+1,03 ± 0,43	+1,07 ± 0,42
	-0,30 ± 0,49	+1,44 ± 0,49	+1,35 ± 0,48	+2,64 ± 0,47	+2,32 ± 0,46	+1,82 ± 0,45	+2,12 ± 0,40
12	-1,42 ± 0,48	-0,34 ± 0,48	-0,55 ± 0,47	-1,49 ± 0,45	-1,27 ± 0,44	-0,78 ± 0,42	-0,80 ± 0,40
	-2,20 ± 0,72	-1,09 ± 0,45	-0,97 ± 0,44	-0,87 ± 0,43	-1,76 ± 0,41	-0,10 ± 0,40	-2,92 ± 0,40

Table 12

Percentage changes in original solution activity of Fe^{59} with time.

Percentage change after

Duplicate number	1 day	2 days	4 days	8 days	16 days	32 days	64 days
1		-2,11 ± 0,82	-0,20 ± 0,81	-4,13 ± 0,80	-2,37 ± 0,78	-3,32 ± 0,74	-2,78 ± 0,69
		+1,15 ± 0,80	-0,07 ± 0,80	-1,47 ± 0,78	-1,81 ± 0,76	-1,93 ± 0,73	-1,37 ± 0,67
2		-0,90 ± 0,81	+2,12 ± 0,81	+0,78 ± 0,79	+2,47 ± 0,77	+3,08 ± 0,74	+0,35 ± 0,68
		+2,10 ± 0,82	+3,15 ± 0,81	+4,62 ± 0,80	-0,78 ± 0,78	+3,66 ± 0,74	+2,04 ± 0,69
3		+5,98 ± 0,85	+2,82 ± 0,84	-1,66 ± 0,82	+5,18 ± 0,81	+2,00 ± 0,77	+5,57 ± 0,72
		+1,95 ± 0,82	+3,02 ± 0,81	+1,28 ± 0,80	-2,88 ± 0,77	-0,39 ± 0,74	-1,94 ± 0,68
4		-5,47 ± 0,81	-3,78 ± 0,81	-3,03 ± 0,80	-0,61 ± 0,78	-1,90 ± 0,74	-3,26 ± 0,69
		-1,77 ± 0,83	-1,65 ± 0,82	-2,53 ± 0,81	-4,78 ± 0,78	-4,74 ± 0,75	-1,99 ± 0,71
5	-1,14 ± 0,50	+1,74 ± 0,50	+3,83 ± 0,50	+2,01 ± 0,49	+3,03 ± 0,58	+4,25 ± 0,46	+2,49 ± 0,42
	-4,32 ± 0,49	+1,00 ± 0,50	-0,04 ± 0,49	-0,66 ± 0,49	-1,34 ± 0,47	+3,41 ± 0,45	+1,77 ± 0,42
6	+1,52 ± 0,52	+3,21 ± 0,52	+2,69 ± 0,51	+2,37 ± 0,50	+0,17 ± 0,49	+6,60 ± 0,47	+4,00 ± 0,43
	-2,88 ± 0,50	-1,11 ± 0,50	-1,35 ± 0,49	-0,23 ± 0,49	-1,20 ± 0,47	-2,18 ± 0,45	-0,45 ± 0,42
7	-2,03 ± 0,36	-0,72 ± 0,36	-1,97 ± 0,35	+0,03 ± 0,35	-2,42 ± 0,34	+3,00 ± 0,32	+3,91 ± 0,30
	+0,31 ± 0,50	+0,27 ± 0,50	-0,59 ± 0,49	+0,69 ± 0,49	-0,24 ± 0,47	+0,12 ± 0,45	+0,05 ± 0,42
8	+0,20 ± 0,51	+2,28 ± 0,51	+1,97 ± 0,50	+3,45 ± 0,49	+2,05 ± 0,48	+3,17 ± 0,46	+3,70 ± 0,43
	-0,45 ± 0,50	+1,53 ± 0,50	-0,05 ± 0,49	+0,81 ± 0,48	-0,29 ± 0,47	+3,46 ± 0,45	+0,57 ± 0,42
9	-0,97 ± 0,51	+1,98 ± 0,51	+0,83 ± 0,50	+2,56 ± 0,49	+1,85 ± 0,48	+2,07 ± 0,45	+1,33 ± 0,42
	-1,08 ± 0,50	-3,95 ± 0,50	+0,11 ± 0,49	-0,27 ± 0,49	-0,83 ± 0,48	0,00 ± 0,47	+0,28 ± 0,45
10	+0,98 ± 0,50	+0,55 ± 0,50	+1,22 ± 0,49	+0,53 ± 0,48	-0,41 ± 0,47	+0,63 ± 0,47	+0,22 ± 0,45
	+1,17 ± 0,51	+0,94 ± 0,51	+3,60 ± 0,50	+2,79 ± 0,49	+3,27 ± 0,47	+1,53 ± 0,45	+2,34 ± 0,44
11	-1,70 ± 0,50	-0,61 ± 0,50	+1,93 ± 0,49	+0,95 ± 0,47	+0,73 ± 0,46	+3,33 ± 0,45	+2,82 ± 0,44
	-0,21 ± 0,50	+0,81 ± 0,50	+1,53 ± 0,50	+2,64 ± 0,49	+1,85 ± 0,47	+1,10 ± 0,45	+2,38 ± 0,45
12	+0,79 ± 0,51	+0,15 ± 0,51	+1,14 ± 0,50	-0,08 ± 0,49	+1,63 ± 0,47	+0,66 ± 0,45	+0,66 ± 0,42
	-2,01 ± 0,72	-1,43 ± 0,72	-0,73 ± 0,71	-0,74 ± 0,70	+1,09 ± 0,69	+0,95 ± 0,65	-1,84 ± 0,60

Table 13

Percentage changes in original solution activity of Zn^{65} with time.

Duplicate number	Percentage change after						
	1 day	2 days	4 days	8 days	16 days	32 days	64 days
1		+1,74 ± 0,69	+1,52 ± 0,69	-0,02 ± 0,68	+1,37 ± 0,68	+0,81 ± 0,67	+1,21 ± 0,65
		+3,52 ± 0,70	+3,13 ± 0,69	-6,19 ± 0,68	-0,06 ± 0,68	+4,71 ± 0,68	+4,48 ± 0,66
2		+5,05 ± 0,71	+7,50 ± 0,71	+3,76 ± 0,70	+5,38 ± 0,70	+4,89 ± 0,69	+2,60 ± 0,67
		+0,22 ± 0,69	+1,38 ± 0,69	+3,97 ± 0,69	+1,32 ± 0,68	+1,20 ± 0,67	-0,31 ± 0,66
3		+3,48 ± 0,76	+3,81 ± 0,76	-3,18 ± 0,74	-3,57 ± 0,75	+2,96 ± 0,74	+2,73 ± 0,72
		-0,12 ± 0,68	+0,26 ± 0,68	-1,60 ± 0,68	-1,10 ± 0,67	-4,13 ± 0,66	-0,10 ± 0,65
4		-1,76 ± 0,69	-0,96 ± 0,69	-0,19 ± 0,69	-1,22 ± 0,68	-1,28 ± 0,68	-1,57 ± 0,66
		+2,64 ± 0,70	+0,77 ± 0,70	+1,50 ± 0,70	-3,37 ± 0,69	+0,84 ± 0,69	-1,45 ± 0,67
5	-1,64 ± 0,97	+1,27 ± 0,98	+2,23 ± 0,98	-0,49 ± 0,96	+0,45 ± 0,96	+3,28 ± 0,95	+0,13 ± 0,91
	-2,18 ± 0,98	+0,49 ± 0,99	-2,92 ± 0,98	-0,92 ± 0,98	+1,57 ± 0,97	+2,78 ± 0,96	+0,20 ± 0,92
6	-1,81 ± 0,98	+2,44 ± 0,99	-1,31 ± 0,98	-1,23 ± 0,97	-0,66 ± 0,97	+1,49 ± 0,95	-6,71 ± 0,91
	-4,42 ± 0,97	-1,13 ± 0,97	-2,52 ± 0,96	-0,17 ± 0,96	-1,33 ± 0,96	-0,25 ± 0,94	-1,67 ± 0,91
7	-1,17 ± 1,10	+3,23 ± 1,11	+2,29 ± 1,10	+0,81 ± 1,09	-0,53 ± 1,08	+3,11 ± 1,05	+5,56 ± 1,02
	+2,36 ± 1,00	+3,70 ± 1,01	+0,75 ± 1,00	+0,96 ± 0,99	+1,11 ± 0,98	-5,47 ± 0,95	+5,33 ± 0,94
8	-0,84 ± 0,98	-0,86 ± 0,98	+1,76 ± 0,98	-0,63 ± 0,97	+0,54 ± 0,96	+3,63 ± 0,93	+3,97 ± 0,92
	-1,73 ± 0,97	+1,05 ± 0,97	+1,81 ± 0,97	-2,72 ± 0,96	-0,15 ± 0,95	+1,46 ± 0,92	-7,71 ± 0,91
9	-3,50 ± 1,00	+2,05 ± 1,00	+2,08 ± 0,99	+1,98 ± 0,99	-0,08 ± 0,97	+4,65 ± 0,95	+0,31 ± 0,93
	+0,36 ± 0,98	-2,88 ± 0,98	-1,32 ± 0,97	-1,26 ± 0,96	+0,74 ± 0,94	+2,44 ± 0,93	-1,88 ± 0,90
10	-0,17 ± 0,97	-1,79 ± 0,97	+1,46 ± 0,96	-0,42 ± 0,95	-0,41 ± 0,94	+1,48 ± 0,93	+2,11 ± 0,90
	+1,68 ± 0,98	+1,93 ± 0,98	+1,46 ± 0,97	+0,23 ± 0,95	+3,44 ± 0,94	+3,24 ± 0,93	+4,06 ± 0,90
11	-2,85 ± 0,96	-1,55 ± 0,96	+0,71 ± 0,95	-4,11 ± 0,94	+0,29 ± 0,92	-0,29 ± 0,92	+1,35 ± 0,90
	-0,86 ± 0,98	+1,69 ± 0,98	-1,39 ± 0,97	+2,10 ± 0,95	-0,81 ± 0,93	+2,86 ± 0,91	+1,39 ± 0,90
12	-1,95 ± 0,97	-0,77 ± 0,97	-1,09 ± 0,96	-3,67 ± 0,95	-2,90 ± 0,93	-0,92 ± 0,91	0,00 ± 0,90
	-0,48 ± 0,91	+0,87 ± 0,91	+0,37 ± 0,90	-0,90 ± 0,87	+0,47 ± 0,86	+2,06 ± 0,85	-5,37 ± 0,84

during which the gamma-ray emission of this isotope is counted, it is not necessary to apply a correction for the natural decay of the isotope during the counting period. The percentage change in the initial activity of the solution after a time t is therefore

$$\left[\frac{(n_{po} - n_{pt}) \pm \sqrt{(\sigma_o)^2 + (\sigma_t)^2}}{n_{po}} \right] \times 100 .$$

where n_{po} is the original nett (peak) activity,

n_{pt} is the corrected nett peak at time t,

and σ_o and σ_t are the respective associated uncertainties.

2.3432 DISCUSSION AND CONCLUSIONS.

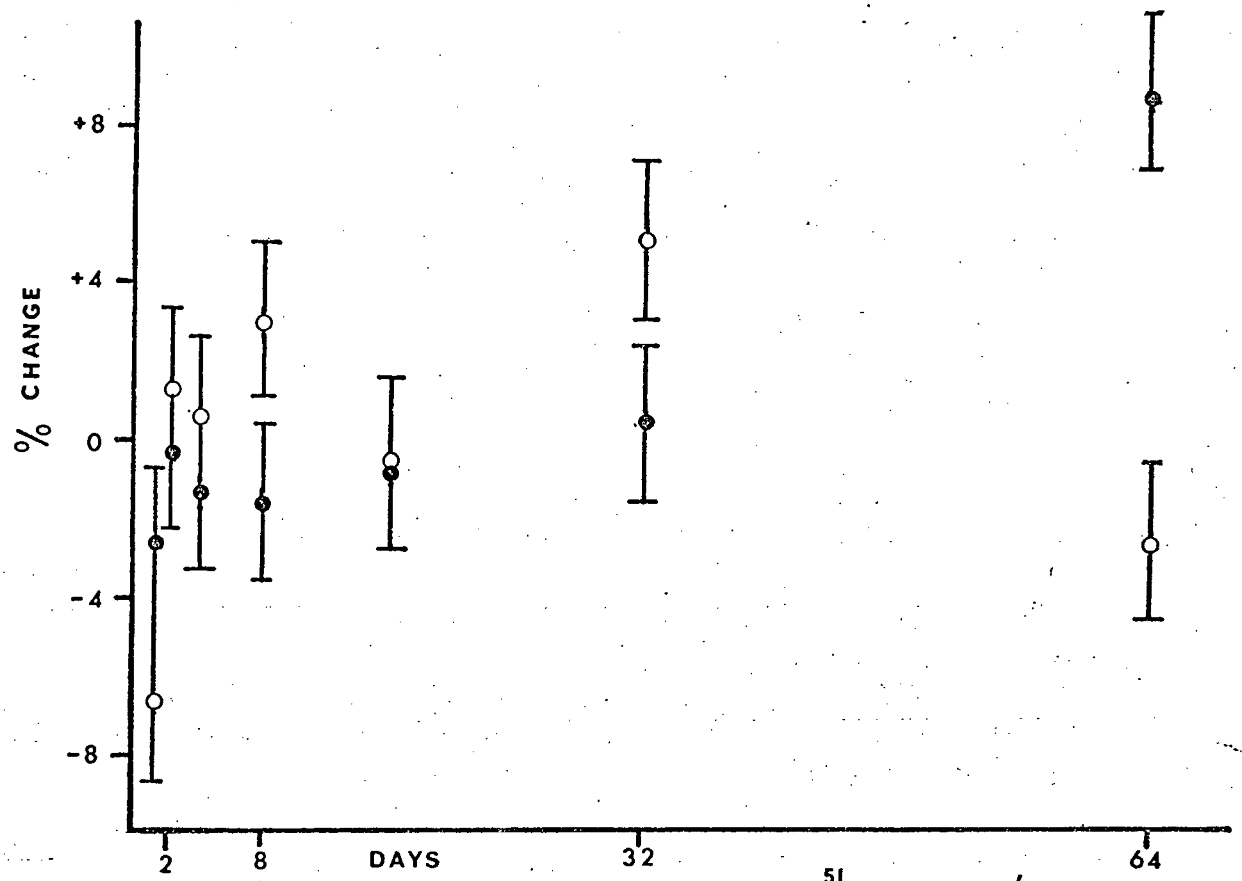
The data are presented in Tables 10 to 13 in the form of the percentage changes in activity, relative to the initial (day zero) measurement, with time. The maximum negative value in any duplicate data set is underlined. For purposes of illustration, some examples are given graphically in Figure 31.

An examination of this data shows that (i) the real nett experimental error exceeds the range of the theoretical counting error. The total real error appears to be of the order of 4% to 8%. (ii) the maximum "observed" change in activity due to adsorption in any sample is only 8,81% (Cr), and in three-quarters of the samples it is less than 5%. This means that the experimental error will make it difficult to distinguish real trends in the data.

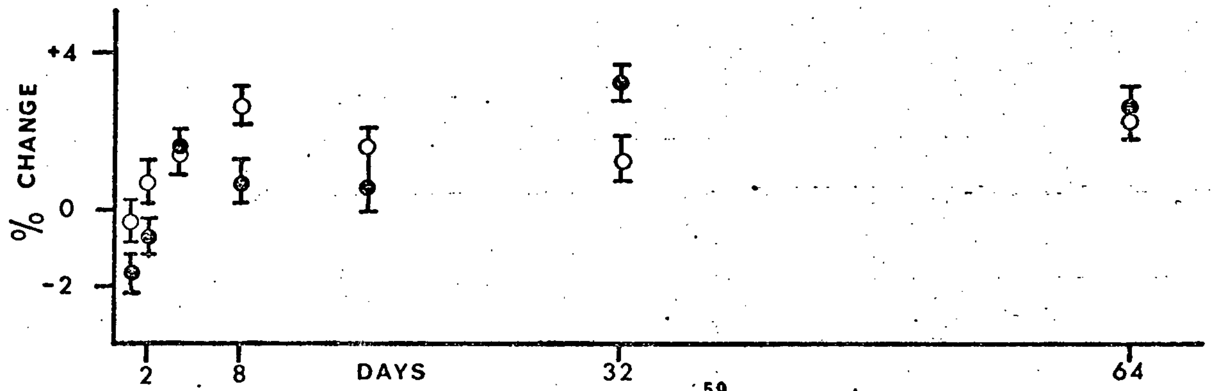
For each data set a regression analysis gave a value for the intercept and the slope of the straight line best fitted to these points, and also a correlation coefficient. A trend was considered to be "real" only if this regression analysis produced similar values for both duplicate data sets. Nett increases in the amount of metal in solution were dismissed as spurious. Only in a handful of cases was there any evidence of a systematic loss of metal from solution with time. These "possible" adsorption trends are summarized in Table 14. In no case is the "possible" trend supported by good correlation coefficents. The most interesting observation about the table is that in all of the samples showing these "possible" adsorption trends the preserving acid is HCl.

Figure 31

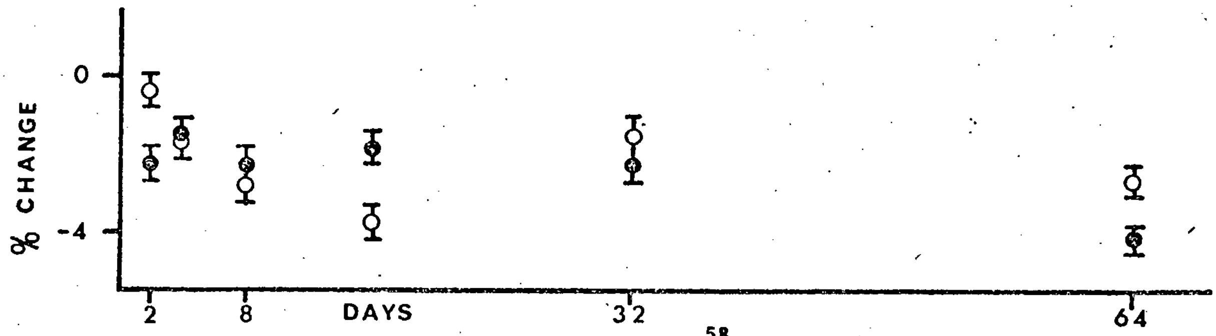
Some graphical representations of percentage changes in original solution activity with time.



EXAMPLE A: RANDOM VARIATION. Cr^{51} Perchloric/Nitric



EXAMPLE B: NETT INCREASE. Fe^{59} Water/Nitric



EXAMPLE C: ADSORPTION. Co^{58} Nitric/Hydrochloric

Table 14

Summary of "possible" adsorption trends.

Element	Pre-cleaning acid	Preserving acid	Approximate apparent loss after 64 days	Correlation
Cr	HNO_3	HCl	5%	poor
Co	HNO_3	HCl	3%	poor
Co	$HClO_4$	HCl	1,5%	poor
Fe	HNO_3	HCl	2,5%	poor
Zn	$HClO_4$	HCl	2%	poor

The one obvious and important conclusion is that for each of the elements studied, at the concentration levels used, the amount of metal lost from solution is less than 10% after 64 days. For most hydrogeochemical purposes such a loss would be regarded as negligible. There is some inconclusive evidence that HCl is the least effective preserving acid, and that the loss of some elements from HCl solutions might have become more readily apparent had the experiment been of longer duration.

It is unfortunate that this experiment could not include the other trace elements of interest in the Karroo project (cf. section 2.33 and 2.34), but this work has shown that the radio-isotopic tracer method is a powerful and practical means of monitoring undesirable adsorption processes in containers intended for storage of hydrogeochemical samples.

2.35 AN AAS STUDY OF THE BEHAVIOUR OF VERY DILUTE (5 μg/1 TO 50 μg/1) SOLUTIONS OF VARIOUS ELEMENTS STORED IN THE GIVEN TYPE OF POLYETHYLENE CONTAINER.

2.351 INTRODUCTION.

The aim of this experiment was to follow, week-by-week, the nett changes in the solution concentration of selected trace elements as a result of concurrent contamination/adsorption phenomena.These tests were conducted in different acid media (HNO_3, HCl, $HClO_4$)and in containers pre-cleaned with different acidic solutions. In accordance with the experience gained from the earlier experiment, some specific changes were made, eg. (i) the solutions were not allowed to contact the closures. Since the polyethylene alone was to be studied, and since almost all authors (section 2.2) agree that polyethylene containers must be acid-rinsed before use, unwashed controls were discarded. (ii) nitric acid of a high purity was used to minimize lead contamination.

The trace elements selected for investigation were cadmium, zinc, thallium, lead, silver, manganese, copper and cobalt. It was not feasible to include uranium in this experiment.

2.352 EXPERIMENTAL METHOD.

Many of the general features of this experiment are similar to those described in section 2.33.

(a) Preparation of containers.

Six new Polykan 57/500 bottles were selected at random from the same batch used in the foregoing experiments. The cardboard sealing liners were removed from each bakelite cap. These six bottles were divided into three groups:

(1) two bottles to be pre-cleaned with hydrochloric acid (Merck 'Pro Analysi')

(2) two bottles to be pre-cleaned with nitric acid (Hopkin and Williams, Analar Grade),

and (3) two bottles to be pre-cleaned with perchloric acid (May and Baker, Reagent Grade).

The bottles were filled with a 70% (v/v) solution of the respective acids*

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*Throughout this experiment the acids used came from the same respective stock bottles.

and stored upright for 24 hours. After this pre-cleaning period, all the bottles were rinsed five times with double-distilled water.

(b) Preparation of sample solutions.

Three sample solutions, each of one litre, were prepared by diluting 1 000 mg/l stock solutions of the elements with pure water and either HCl, HNO_3 or $HClO_4$ (finally at a theoretical pH of 1,0). Each of these three dilute, acidified solutions contained all of the elements studied, in the following concentrations: Cd 5 µg/l, Zn 5 µg/l, Tl 50 µg/l, Pb 10 µg/l, Mn 10 µg/l, Ag 5µg/l. Cu 10 µg/l and Co 20 µg/l.

After being shaken, the samples were split to give duplicates. The two polyethylene bottles which had been pre-cleaned with HCl were filled with equal volumes of the HCl sample solution, and the procedure was repeated, mutatis mutandis,for the HNO_3 - and $HClO_4$ - cleaned containers.

(c) Preparation of calibration standards.

In this experiment the problem of standardization was not as severe as it was in the earlier contamination study (section 2.33), because the samples were spiked with easily measureable masses of elements. Therefore a permanent control standard was not neccessary and fresh standards were conveniently prepared each week. An adjustable pipette with disposable plastic tips (Gilson Pipetman P 200) was used to inject the appropriate microlitre volume of the 1 000 mg/l commercial standards into one-litre volumetric flasks. The concentrations of the elements in the standards were the same as those listed in (b) above.

(d) Analysis.

The AAS analytical procedures were essentially the same as those described in section 2.322. The control standards were analysed at regular intervals throughout each run to monitor instrumental drift.

Analysis of each sample and control standard was repeated until three concordant absorbance values were obtained. The mean of at least three values was taken as the final result in each case.

The concentration of any given element in the sample solutions was determined by direct comparison of the absorbance values of the samples and control standards.

2.353 RESULTS AND DISCUSSION

The duplicates showed excellent agreement, with maximum differences of 2 µg/l for any comparable pair of samples. Tables 15 to 17 therefore show only the mean values obtained for the various test solutions. The following is apparent from this data:

(1) There is no nett contamination of any element in any sample. This is in agreement with the results of the foregoing experiments, from which it was predicted that the closures of the Polykan containers were the principal source of contamination and that the polyethylene was unlikely to cause problems.

(2) Nitric acid is clearly the preferred preservative. Within the limits of experimental error, no serious changes in the concentration of any element can be discerned. It should be noted that these results are apparently in conflict with the observations of section 2.33 (see Figures 10 and 13) where an amount of (acid blank) lead equivalent to a concentration of about 4 µg/l "disappeared" from solution over a period of eight weeks. The factors controlling adsorption processes may be quite subtle /56/, and it should be noted that the two experiments, although similar in many respects, were <u>not</u> identical. It is therefore pointless to speculate here about the cause of this inconsistency, which could only be properly resolved by further experimental work that is considered to be beyond the scope of this thesis.

(3) The other two acids were less successful as preservatives. Thallium was rapidly lost from HCl solutions. Otherwise, there is nothing in the data to confirm the earlier suggestion (section 2.3432) that the hydrochloric acid might be a relatively poor preserver of dilute solutions of Co and Zn. Thallium, Cd, Mn, Ag and perhaps Co were all lost from $HClO_4$ solutions.

(4) There is some suggestion of real week-to-week fluctuations in the concentrations of some elements in certain samples. However, these variations may be no more than experimental error and in the absence of more definite data these apparent changes cannot be meaningfully interpreted.

2.36 INFRA-RED SPECTROSCOPIC AND ELECTRON-MICROSCOPIC STUDY OF POLYETHYLENE.

2.361 INFRA-RED SPECTROSCOPY.

Although it is generally agreed that polyethylene is "inert" to acidic attack /60/, the writer decided to see if sensitive techniques would detect changes in polyethylene surfaces exposed to different acids.

Table 15

Behaviour of elements in a nitric acid medium.

(all values in μg/1)

Element	Week								
	0	1	2	3	4	5	6	7	8
Cd	5,0	4,5	3,4	3,6	6,1	6,3	6,0	5,7	6,2
Zn	5,0	3,2	3,3	5,1	6,0	4,8	4,4	4,6	7,1
Tl	50,0	40,9	40,5	41,8	57,0	54,3	51,6	58,7	59,3
Pb	10,0	4,6	4,9	10,2	10,6	12,3	8,7	14,0	11,5
Mn	10,0	9,0	7,4	6,7	6,9	10,0	10,3	8,5	11,1
Ag	5,0	2,8	4,0	4,2	3,7	4,3	5,0	5,4	6,0
Cu	10,0	5,9	9,4	7,8	8,1	8,0	8,3	9,7	11,1
Co	20,0	13,3	17,2	10,9	13,6	16,3	18.1	21,0	15,8

Table 16

Behaviour of elements in a hydrochloric acid medium.

(all values in µg/1

Element	Week 0	1	2	3	4	5	6	7	8
Cd	5,0	1,1	4,2	3,8	6,2	5,1	5,0	5,4	6,3
Zn	5,0	2,1	2,7	5,0	5,0	5,2	4,7	4,9	7,2
Tl	50,0	1,8	1,6	1,5	3,8	8,0	5,5	8,0	6,3
Pb	10,0	4,3	9,7	10,5	13,3	10,8	8,7	11,1	9,6
Mn	10,0	3,3	7,0	6,5	7,4	9,1	7,9	9,3	10,0
Ag	5,0	2,9	3,1	4,0	5,2	4,1	4,2	3,6	5,5
Cu	10,0	7,2	9,0	7,3	8,1	9,0	9,1	9,5	11,1
Co	20,0	16,6	20,1	16,5	17,9	22,0	22,2	17,6	20,3

Table 17

Behaviour of elements in a perchloric acid medium.

(all values in µg/1)

Element	Week								
	0	1	2	3	4	5	6	7	8
Cd	5,0	2,3	1,1	1,0	1,4	2,2	2,0	2,3	2,1
Zn	5,0	2,2	1,6	3,0	5,3	4,4	3,7	3,5	5,2
Tl	50,0	2,4	2,7	1,8	1,9	3,0	3,3	2,4	1,3
Pb	10,0	2,9	5,0	7,3	8,1	8,2	6,9	10,1	8,3
Mn	10,0	2,7	2,5	2,9	3,6	6,3	4,5	6,1	5,3
Ag	5,0	2,6	1,5	2,0	2,1	2,4	3,0	3,3	2,1
Cu	10,0	6,5	6,7	7,2	8,3	6,4	6,9	10,5	12,0
Co	20,0	17,7	16,8	10,5	11,6	15,1	14,0	14,3	16,4

Eight (4 x 2 duplicates) circular discs about 2,5 cm in diameter were cut from two Polykan 57/500 containers. Six (3 x 2 duplicates) of these discs were totally immersed in concentrated HNO_3, HCl and $HClO_4$ respectively for four weeks. The fourth pair of discs were kept as blanks.

The infra-red spectra of the eight discs were recorded using a Beckman IR 12 infra-red spectrometer (with fixed conditions in all cases) over the range 1 100 to 2 200 cm^{-1}. In addition, frequencies between 700 to 1 100 cm^{-1} and 3 000 to 4 000 cm^{-1} were scanned on the blank discs only. In each of the four sets of discs the duplicate spectra were identical. These spectra are reproduced in Figures 32 to 36. Figures 37 and 38 are reproduced from Haslam *et al.* /75/ and show spectra of high-pressure polythene and "impure" high-pressure polythene containing residual double bonds, resulting in chain unsaturation.

A comparison of Figures 32 and 33 with Figures 37 and 38 shows that Polykan 57/500 "high-density" polyethylene (HDPE) has characteristics typical of "impure" HDPE, in which there are residual double bonds, chain-unsaturation and polymer branching /60, 75, 76/.

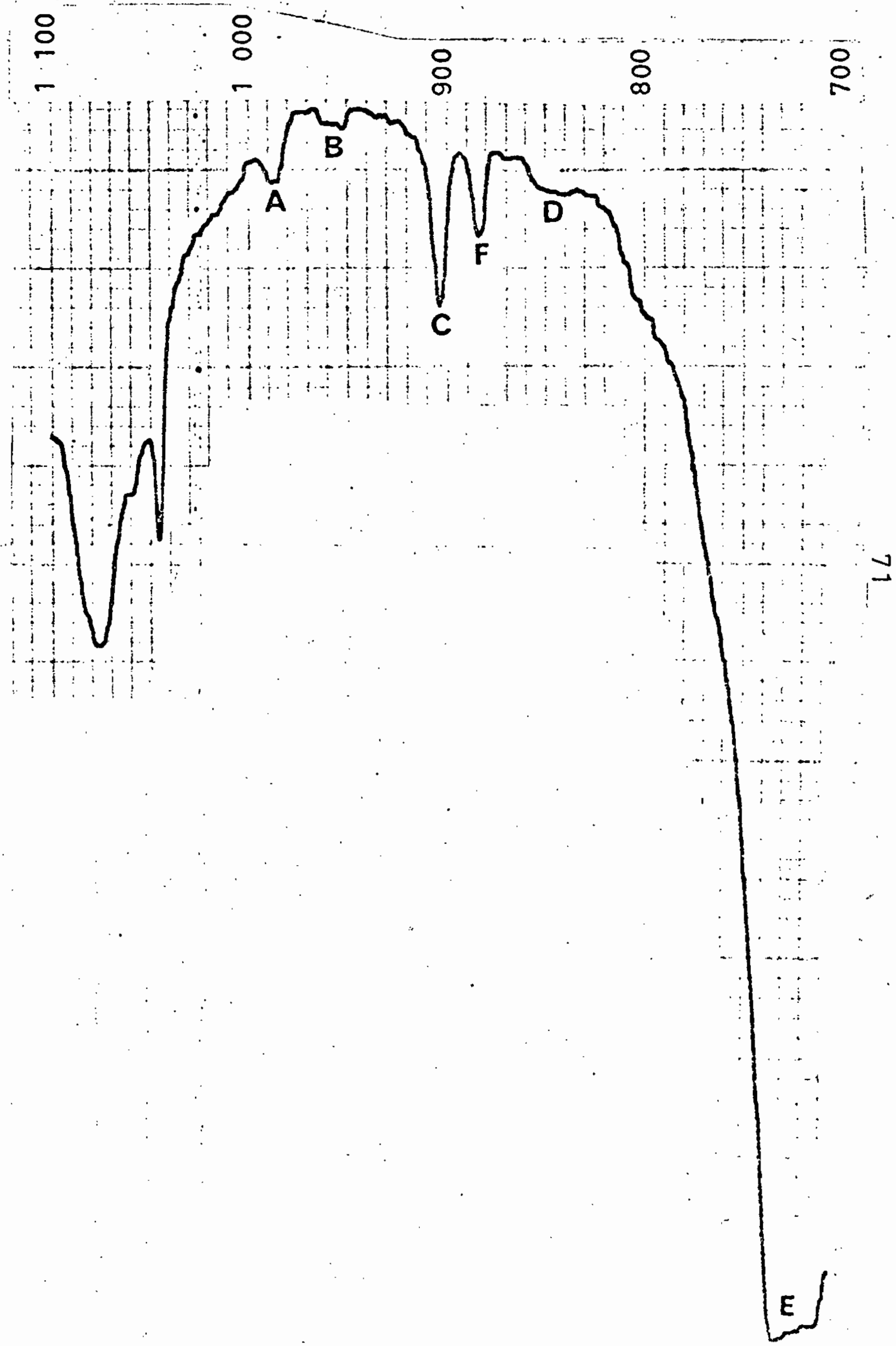
The most useful area of an IR spectrum for detection of unsaturation and branching in a polymer is in the frequency range 700 to 1 100 cm^{-1} /75/. The absorption bands marked A,B,C,D and E between 800 and 1 000 cm^{-1} in Figure 32 are due to unsaturation of the polymer chain and are caused by olefinic double bonds /76/. The assignments of these peaks are given in Table 18. Further evidence of unsaturation in the polymer chain is given by the peaks labelled H, I and J in Figure 33, which result from the presence of olefinic double bonds (J), and C=C stretching modes (H, I).

Branching of a linear polymer chain is shown by the presence of the terminal methyl molecules of pendent alkyl groups containing four or more carbon atoms along the branch. The absorption band labelled F in Figure 32 is evidence for branched polymer chains in Polykan 57/500 polyethylene. In addition, the band at about 1 379 cm^{-1} (labelled G in Figure 33) is caused by methyl groups /76/.

Figures 32 and 33 indicate that new, unused Polykan 57/500 containers consist of polyethylene which is already slightly oxidized at the surface. In figure 32, hydroxyl groups are indicated by an intense peak labelled K, which appears at about 3 600 cm^{-1}, and by weaker peaks labelled L and M at 3 640 and 3 360 cm^{-1}. Oxidation of the polyethylene may occur under the influence of heat or light /75, 76/. It is to be expected that other oxygen-containing groups such as carbonyls and carboxyls are also present /76/.

Figure 32

Infra-red spectrum of polyethylene blank in the regions 700 to 1 100 cm^{-1} and 3 000 to 4 000 cm^{-1}.



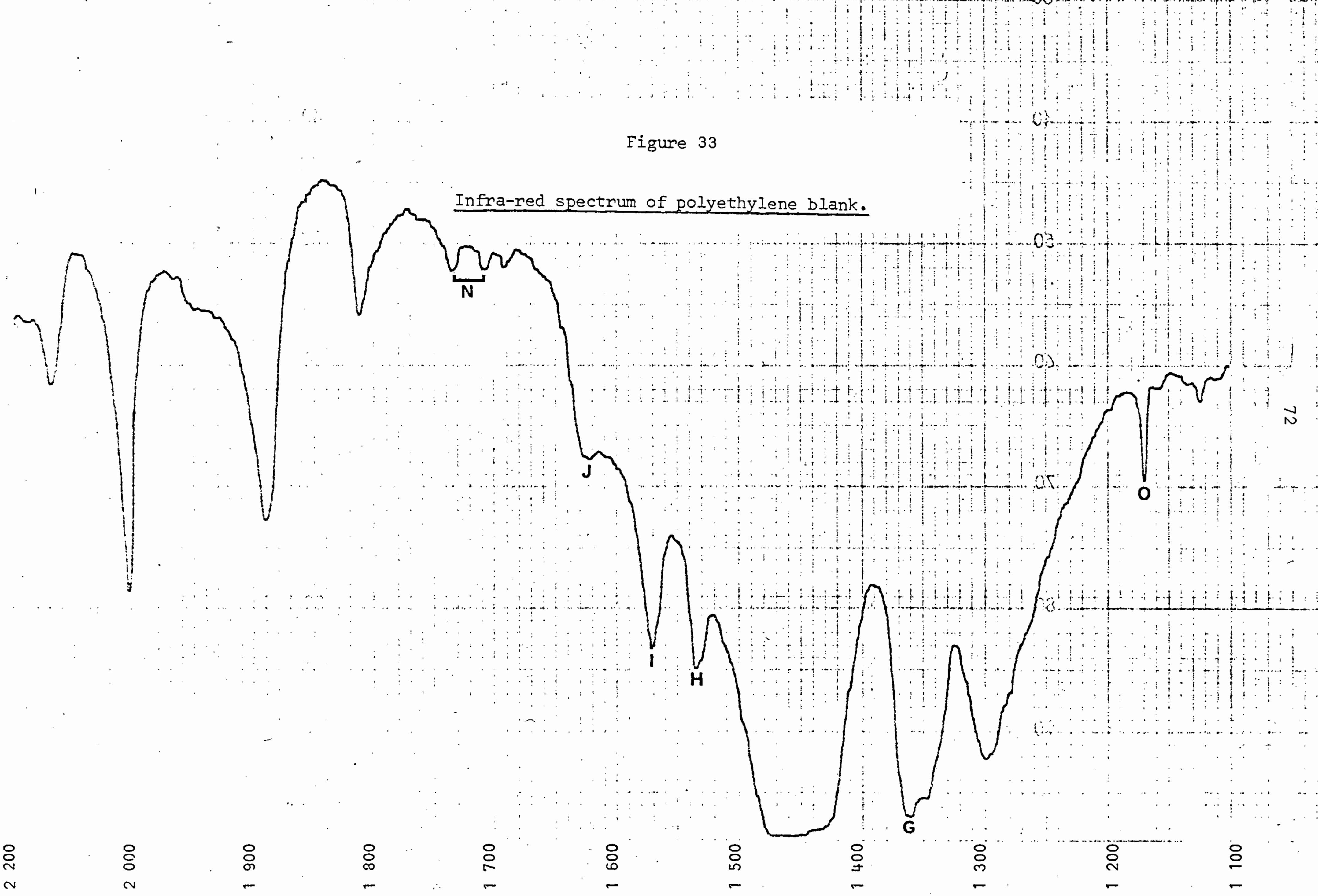


Figure 33

Infra-red spectrum of polyethylene blank.

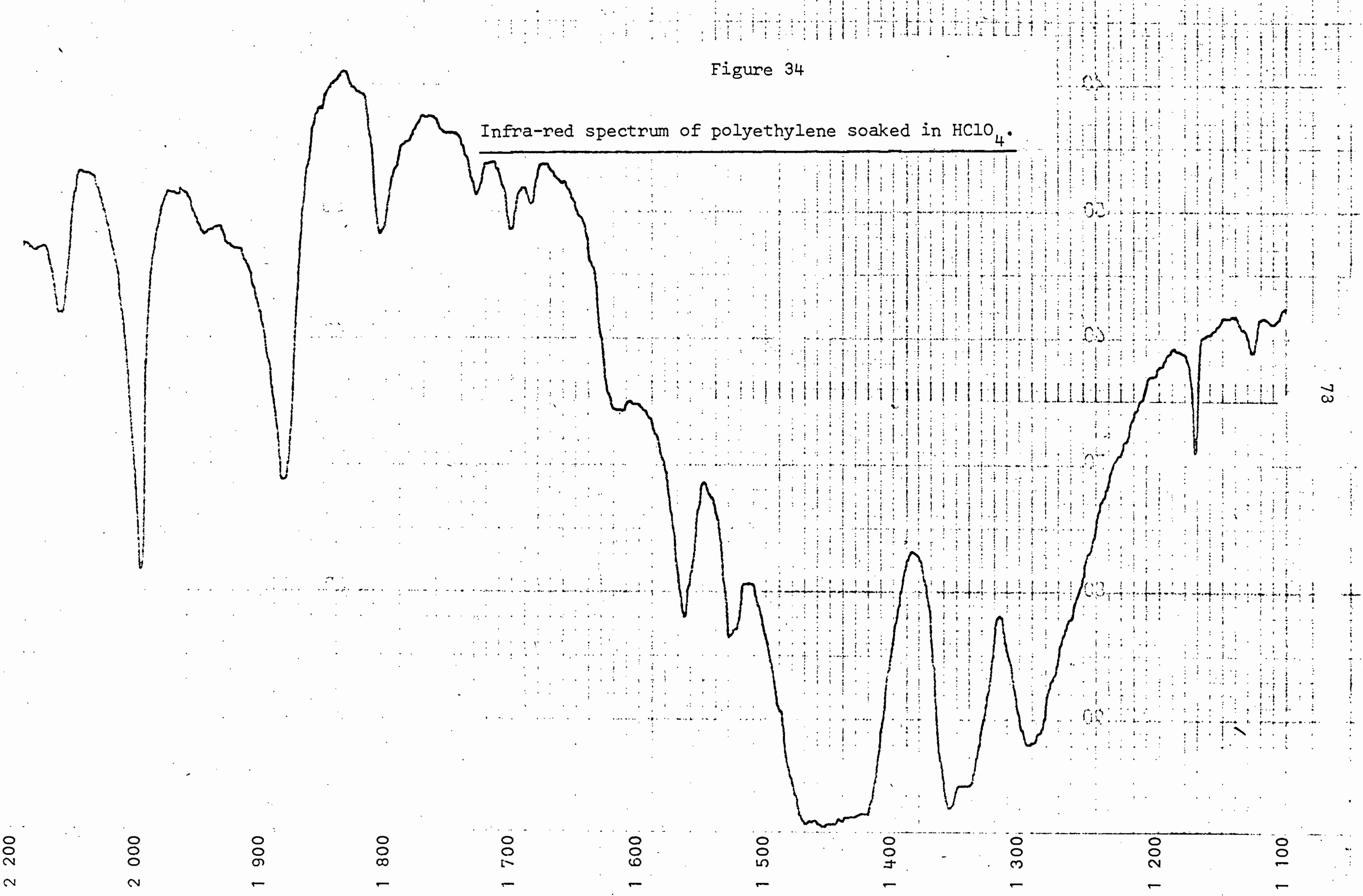


Figure 34

Infra-red spectrum of polyethylene soaked in $HClO_4$.

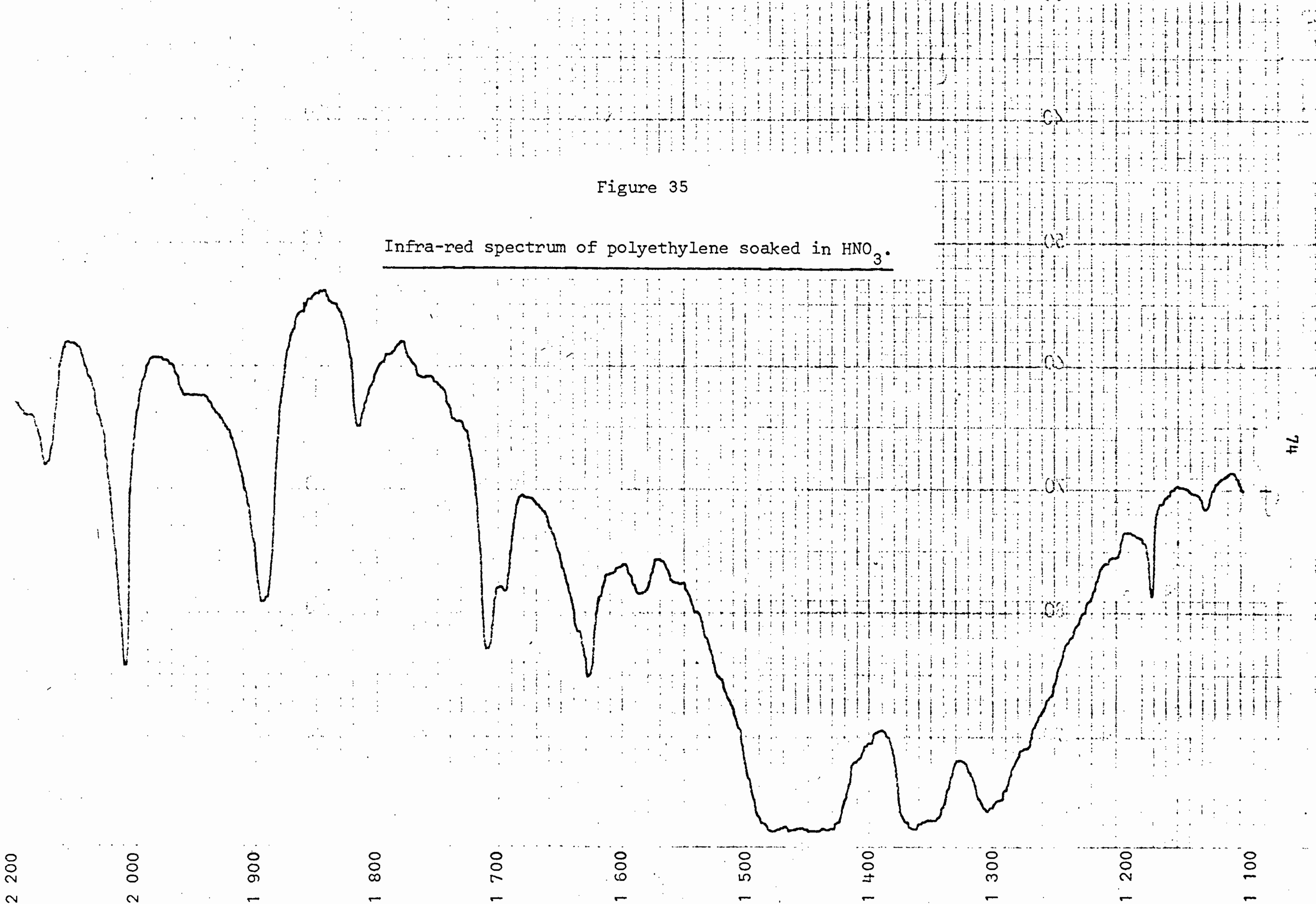


Figure 35

Infra-red spectrum of polyethylene soaked in HNO_3.

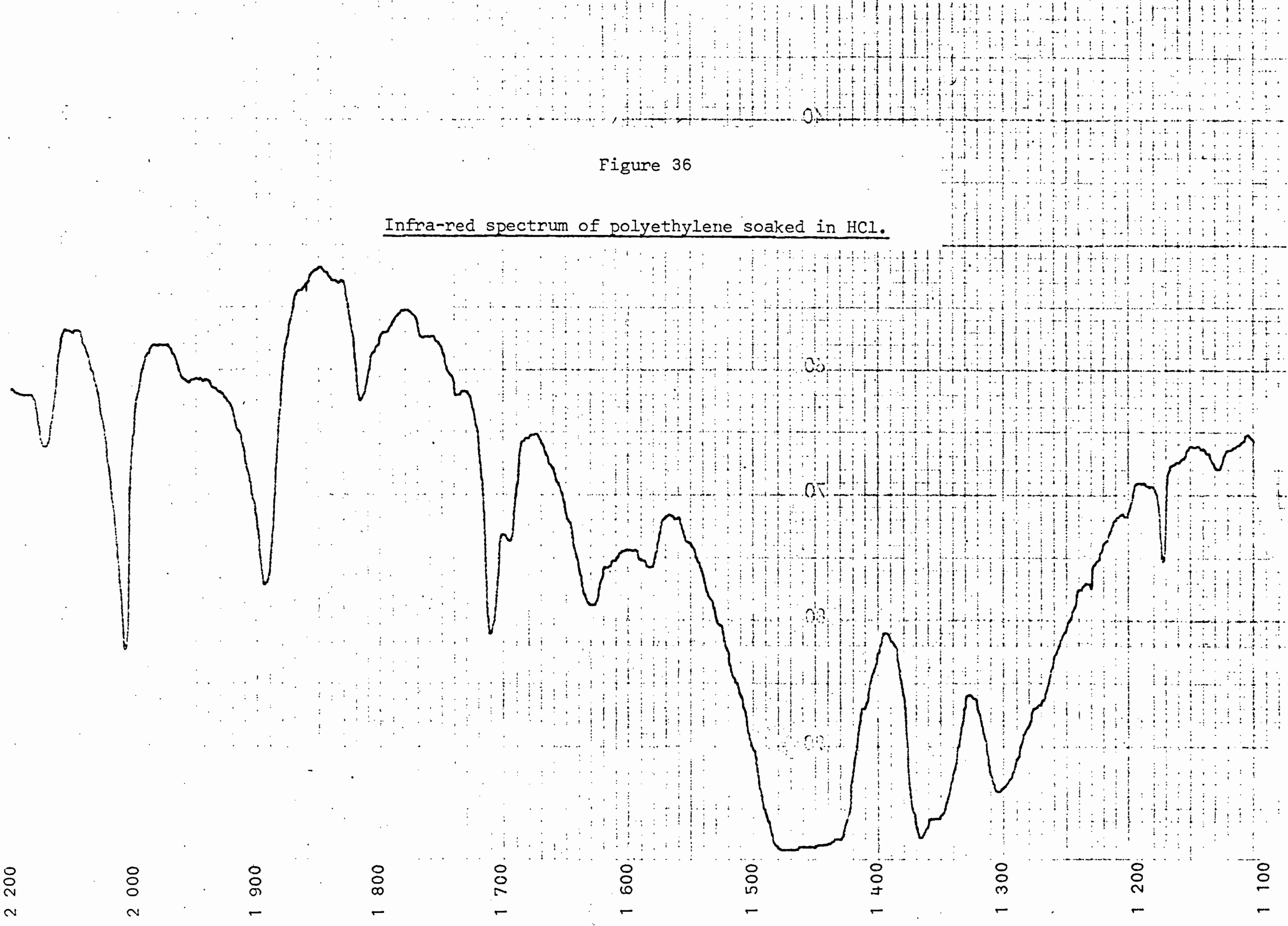
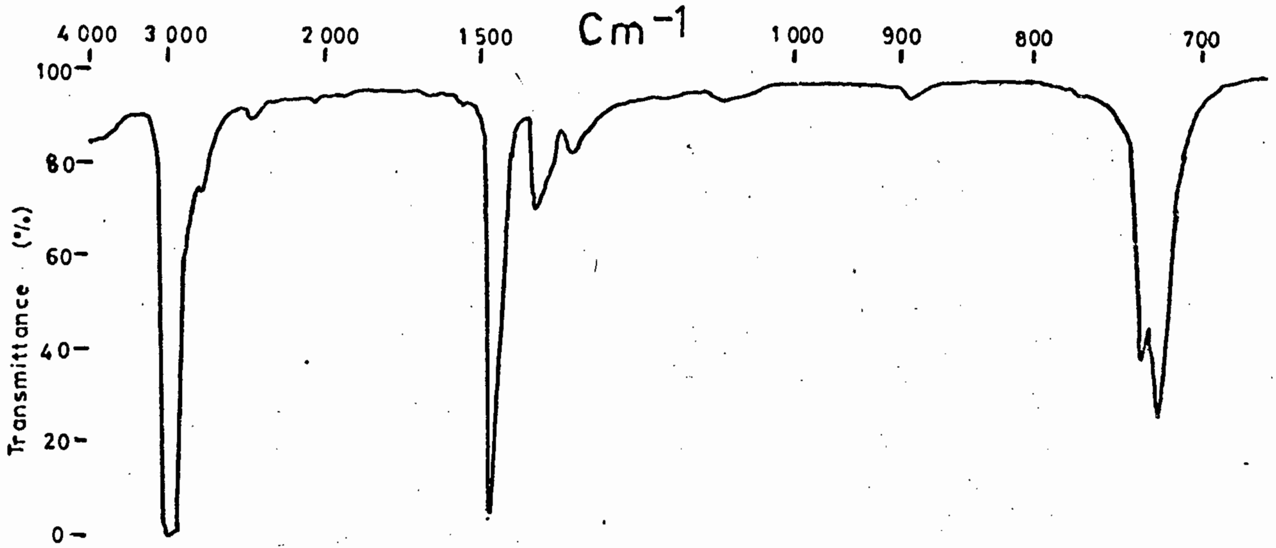


Figure 36

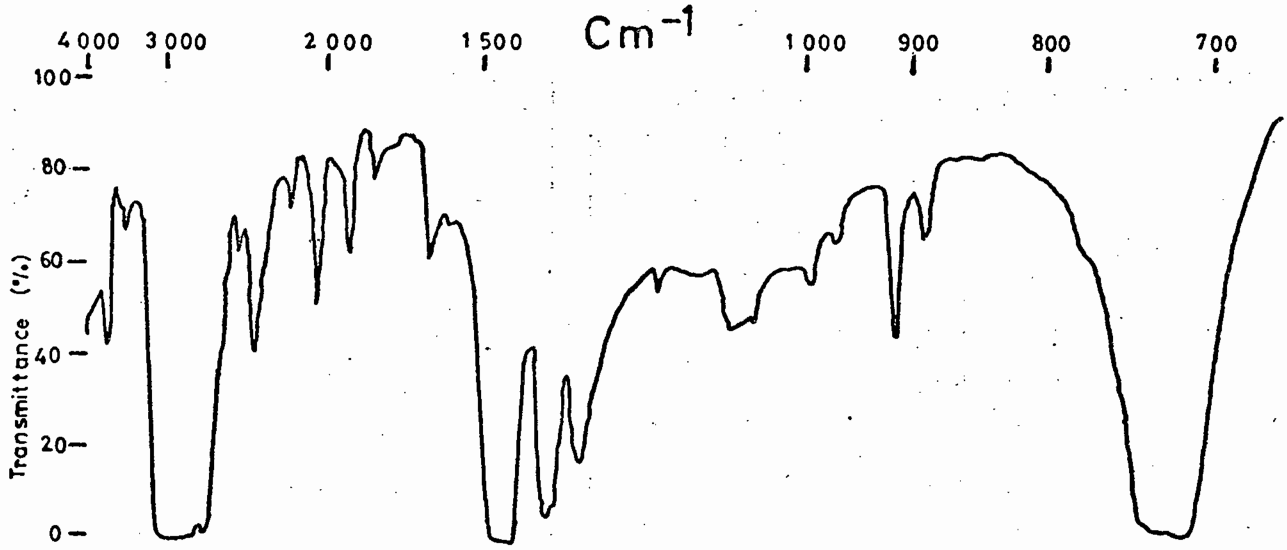
Infra-red spectrum of polyethylene soaked in HCl.

Figure 37



IR spectrum of high-pressure polythene (reproduced from /75/).

Figure 38



IR spectrum of polythene with terminal, pendent-methylene and chain unsaturation (prepared with Ziegler type catalyst) Type "Carlona 800". (reproduced from /75/).

Table 18

Assignment of peaks in the infra-red spectra described in the text.

(from /68, 75, 76/)

Figure	Figure	Label	Assignment
	33	A	$R.CH = CH_2$
	33	B	trans $R.CH = CH.R'$
	33	C	$R.CH = CH_2$
	33	D	$RR'C = CHR''$
	33	E	cis $R.CH = CH.R'$
	33	F	$RR'C = CH_2$
	34	G	$RR'C = CH_2$
	34	H	C = C stretching mode
	34	I	C = C stretching mode
	34	J	$R.CH = CH_2$
	33	K	free hydroxyl groups
	33	L	primary, secondary or tertiary hydroxyl groups associated with an alcohol
	33	M	polymeric hydroxyl groups
	34	N	aldehydic or ketonic carbonyl groups, and carboxyl groups
	34	O	C - O vibration mode of the carboxyl group

Figure 33 shows the presence of a few weak absorption bands (labelled N) at about 1 720 cm^{-1}. These bands occur at the characteristic frequency of aldehydic or ketonic carbonyl groups. In addition, carboxyl groups absorb at about the same frequency, but in some cases it may be difficult to distinguish between the presence of these two main groups /76/. However, if carboxyl groups are present, a band near 1 200 cm^{-1}, due to the C-O vibration within the carboxyl group, must also be present. The band labelled O in Figure 33 might confirm the presence of carboxyl groups. However, since the intensities of the bands labelled N are weak, there is probably not a very large proportion of carbonyl and/or carboxyl groups present. This is to be expected if the polyethylene is not very oxidized.

The presence of at least some proportion of carbonyl and/or carboxyl groups in new, unused Polykan 57/500 polyethylene deserves special mention here, because the tendency of polyethylene surfaces to adsorb trace metals from water samples (see section 2.2) might be due to these groups. Riley (/30/, p. 303) states that: "........surfaces of plastics under the influence of oxygen, heat or light may become degraded with the formation of carboxyl or carbonyl groups which may show adsorptive properties."

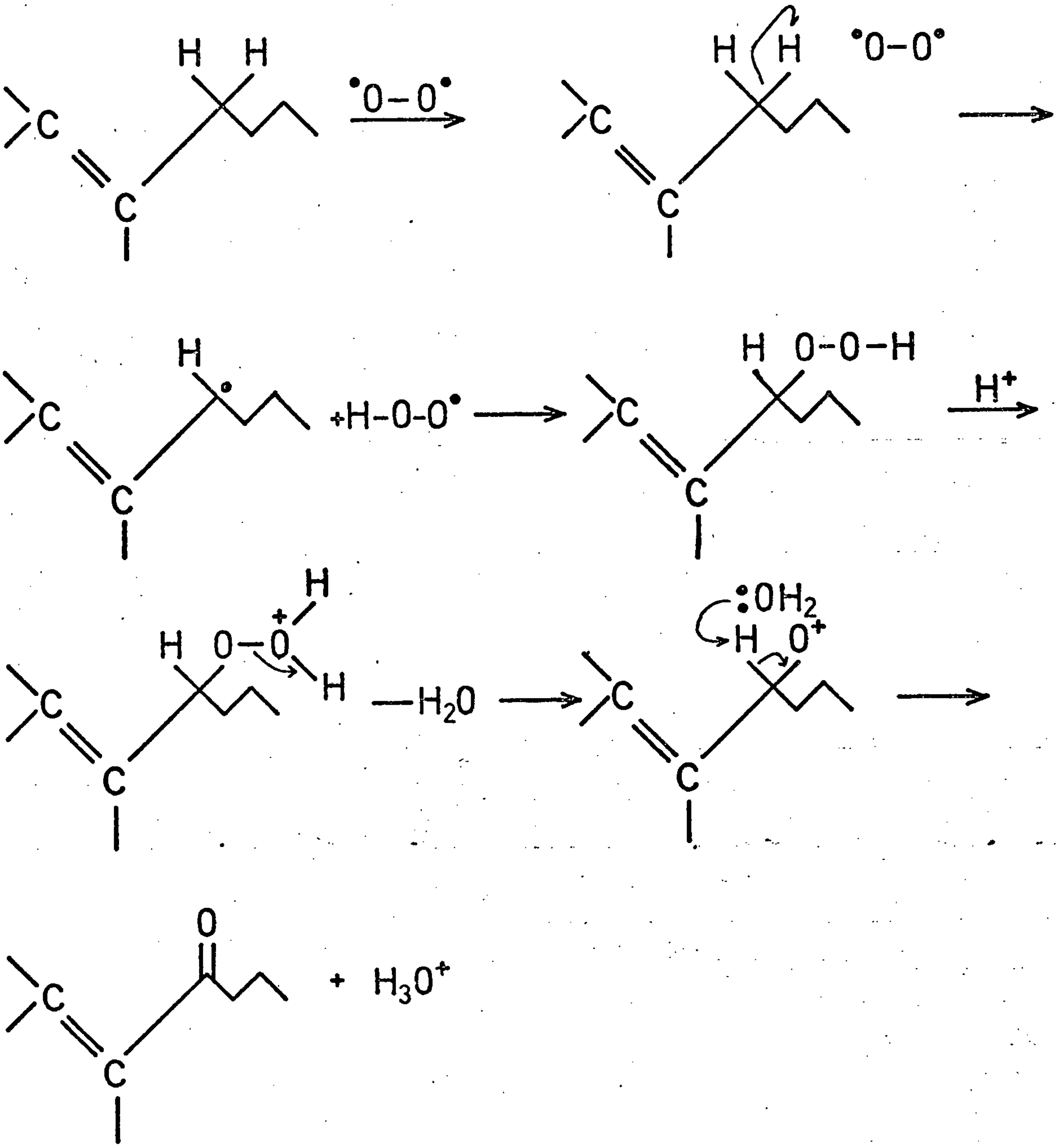
The spectrum of polyethylene soaked in $HClO_4$ (Figure 34) shows very similar features to that of the blank (Figure 33) in the range 1 100 to 2 200 cm^{-1}, except that the bands around 1 720 cm^{-1} became more intense. This indicates slight additional oxidation of the polyethylene and the formation of a larger proportion of carbonyl and/or carboxyl groups. This is not amazing, since Cross *et al.* (/76/, p. 236) state: "The double bonds in ethylene polymers are normally present to the extent of, as a maximum, only one per molecule and have little effect on physical properties, but may be, of course, a centre of sensitivity to chemical attack in, for example, oxidative deterioration." The acid-catalysed formation of carbonyl groups can occur via a mechanism of the type shown in Figure 39.

In addition to the "centres of sensitivity to chemical attack", namely the double bonds in the unsaturated polymer chain, the presence of easily-oxidized hydroxyl groups contributes to the deterioration of the polyethylene surfaces.

The spectra of polyethylene soaked in HNO_3 and HCl (Figures 35 and 36 respectively) resemble each other, but contrast sharply with those of untreated or $HClO_4$ - soaked polyethylene (Figures 33 and 34 respectively). The most significant difference is that the intensity of the absorption band around 1 720 cm^{-1} has increased dramatically in the HNO_3 - and HCl - treated spectra, thereby indicating the presence of a very significant proportion of carbonyl

Figure 39

Mechanism for acid-catalysed carbonyl-group formation.



and / or carboxyl groups. In the case of HNO_3, this could be attributed to the efficiency of this acid as an oxidizing agent. However, it is difficult to imagine why such a large proportion of C=0 bonds should be formed by HCl attack. Several chemists at both the University of Cape Town and the University of Stellenbosch were consulted personally about these observations, but none was able to suggest any reasonable explanation of this phenomenon.

All that can be said at this juncture is that HNO_3 and HCl apparently cause oxidative deterioration of the polyethylene surfaces, and that these changes may be important in determining the behaviour of dissolved trace elements subsequently contacting these surfaces. It seems probable that one could "overexpose" polyethylene to acids and thus cause changes which would later be deleterious to trace element solutions.

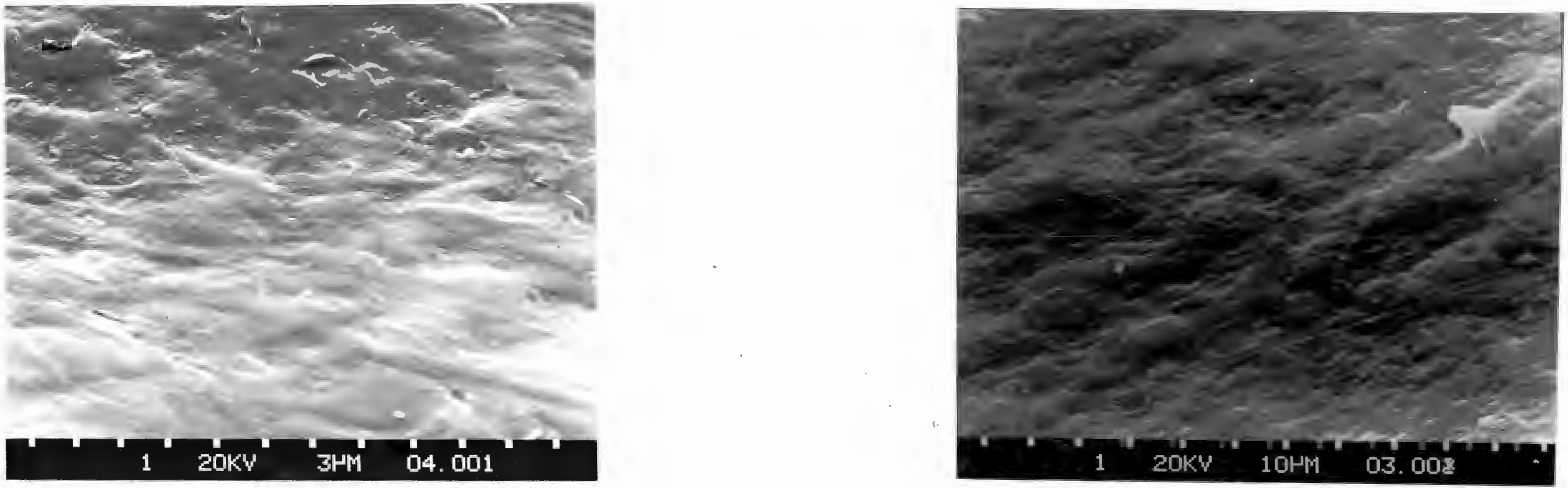
2.362 ELECTRON MICROSCOPY.

The surfaces of the polyethylene discs described in section 2.361 were examined under a scanning electron microscope (SEM) to see if any visible changes were apparent.

Photomicrographs of the surfaces (Figure 40) do not reveal any significant differences between the four surfaces at the magnification used on the SEM.

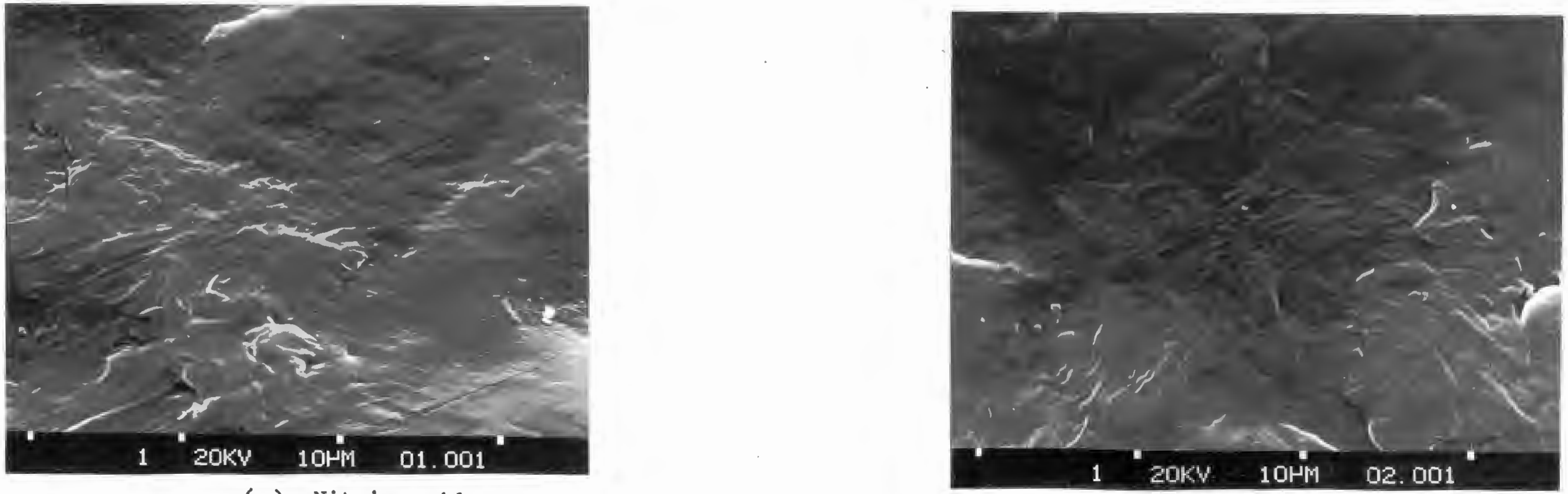
Figure 40

Photomicrographs of polyethylene soaked in various acids.



(a) blank

(b) Perchloric acid



(c) Nitric acid

(d) Hydrochloric acid

3. OVERALL CONCLUSIONS.

The Polykan 57/500 containers can be used for storing hydrogeochemical samples. The containers should be pre-cleaned with 10% HNO_3 for about twenty four hours, but preferably not for longer periods or with stronger acids. The closure must not be exposed to acids.

Very high purity nitric acid should be added to lower the pH to 1,0 and the samples should preferably be frozen /30, 31, 42, 43/.

Under these conditions the small concentrations of the elements Cd, Zn, Tl, Pb, Mn, Ag, Cu and Co and perhaps others should remain unchanged for at least eight weeks. In addition, the containers will not adsorb Fe or Cr, and are U- free.

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APPENDIX 1

Additional technical data on Polykan 57/500 containers.

These containers are manufactured by a blow-moulding process by Polykan Containers, P.O.Box 10390, Johannesburg. No pigments have been added, so that the colour is that of natural high-density polyethylene (HDPE). They can be identified as HDPE bottles by their opaque character, whereas low-density types are non-opaque.

As far as could be ascertained from the manufacturers, no mould-releasing agents such as zinc stearate are used during the moulding process, in which steel, aluminium or stainless steel moulds are used.

The HDPE raw material used for manufacture of the Polykan 57/500 containers is produced by South African Polyolefins (Pty) Ltd., Sasolburg. According to Diedrich and Kort /74/, a highly active titanium-bearing catalyst is used for polymerization. This catalyst is prepared in batches by a simple process from easily obtainable raw materials. Polymerization of ethylene takes place in a reactor at temperatures between 80 to 90 °C and at pressures below 1 MPa after addition of small quantities of other olefins, such as propylene, butene- (1) or hexene- (1), and traces of hydrogen together with the catalyst and a hydrocarbon diluent. The polymer is obtained in the form of a powder suspended in the diluent, which is separated by centrifuging and recycled directly to the polymerization reactor without any purification. The final removal of the diluent from the polymer powder is performed either by direct drying with hot nitrogen, or steam stripping and hot air drying. The dried powder is then extruded into pellets.

The raw HDPE is supplied in this granular form to Polykan Containers. The type used for manufacture of the Polykan 57/500 containers is designated GD 7660 (density = 0,960 g/cm^3) or GF 7650 (density = 0,947). The former type is used mainly for the manufacture of small bottles, while the latter type is used for containers which are to be used for storing materials like detergents.

A description of the manufacturing process used for specific containers can be very useful to the geochemist investigating the suitability of polyethylene bottles for storage of hydrogeochemical samples. For example, if it is known that zinc stearate is used as a mould releasing agent, then it is highly possible that contamination by zinc from the finished product would be very serious. In addition, knowledge of the composition of the catalyst used for polymerization may enable one to predict which elements are likely to be present in the HDPE in relatively large amounts.

APPENDIX 2

Week-by-week sample/standard absorbance ratios and nominal concentrations of the trace elements in the samples investigated in section 2.33.

(In each case the values given in brackets are nominal concentrations in μg/l.)

CADMIUM

Acid Treatment	Week 0	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8
HCl/HCl	0,02	0,03	0,04	0,03	0,10	0,06	0,06	0,14	0,05
	(0,1)	(0,2)	(0,2)	(0,2)	(0,5)	(0,3)	(0,3)	(0.7)	(0,3)
HCl/none	0,02	0,02	0,03	0,03	0,04	0,02	0,02	0,02	0,03
	(0,1)	(0,1)	(0,2)	(0,2)	(0,2)	(0,1)	(0,1)	(0,1)	(0,2)
HNO_3/HNO_3	0,07	0,11	0,08	0,10	0,13	0,13	0,14	0,10	0,13
	(0,4)	(0,6)	(0,4)	(0,5)	(0,7)	(0,7)	(0,7)	(0,5)	(0,7)
HNO_3/none	0,01	0,01	0,01	0,01	0,02	0,02	0,02	0,02	0,01
	(0,1)	(0,1)	(0,1)	(0,1)	(0,1)	(0,1)	(0,1)	(0,1)	(0,1)
none/HCl	0,01	0,00	0,01	0,01	0,02	0,02	0,02	0,07	0,09
	(0,1)	(0,1)	(0,1)	(0,1)	(0,1)	(0,1)	(0,1)	(0,4)	(0,5)
none/HNO_3	0,15	0,12	0,07	0,10	0,11	0,13	0,13	0,08	0,09
	(0,8)	(0,6)	(0,4)	(0,5)	(0,6)	(0,7)	(0,7)	(0,4)	(0,5)
none/none	0,03	0,03	0,01	0,02	0,01	0,01	0,02	0,03	0,02
	(0,2)	(0,2)	(0,1)	(0,1)	(0,1)	(0,1)	(0,1)	(0,2)	(0,1)

ZINC

Acid Treatment	Week 0	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 12
HCl/HCl	0,79	6,67	4,17	2,22	4,76	3,70	5,56	2,44	2,50	
	(4)	(>5)	(>5)	(>5)	(>5)	(>5)	(>5)	(>5)	(>5)	(226)
HCl/none	0,79	3,33	2,33	1,03	1,12	1,16	0,85	1,37	0,93	
	(4)	(>5)	(>5)	(5)	(6)	(6)	(4)	(7)	(5)	(37)
HNO_3/HNO_3	0,85	4,76	3,45	5,88	4,17	3,45	4,76	3,13	4,76	
	(4)	(>5)	(>5)	(>5)	(>5)	(>5)	(>5)	(>5)	(>5)	(79)
HNO_3/none	0,79	3,33	2,63	3,70	3,23	2,86	3,45	2,38	3,45	
	(4)	(>5)	(>5)	(>5)	(>5)	(>5)	(>5)	(>5)	(>5)	(31)
none/HCl	0,18	3,13	2,08	0,52	0,90	2,13	1,15	1,64	1,32	
	(1)	(>5)	(>5)	(3)	(5)	(>5)	(6)	(>5)	(>5)	(59)
none/HNO_3	0,15	3,85	2,63	4,55	3,23	3,03	4,17	3,45	3,85	
	(1)	(>5)	(>5)	(>5)	(>5)	(>5)	(>5)	(>5)	(>5)	(48)
none/none	0,12	0,33	0,31	0,33	0,55	0,28	0,52	0,94	0,41	
	(1)	(2)	(2)	(2)	(3)	(1)	(3)	(5)	(2)	(<5)

For Zn the curvature of the absorbance/concentration plot is so severe that nominal values >5 will be grossly in error. The nominal values in these cases are probably of the order of 20 to 200 µg/l.

THALLIUM

Acid Treatment	Week 0	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8
HCl/HCl	0,05	0,05	0,03	0,00	0,02	0,00	0,02	0,01	0,02
	(5)	(5)	(3)	(<1)	(2)	(<1)	(2)	(1)	(2)
HCl/none	0,01	0,05	0,02	0,00	0,02	0,00	0,02	0,01	0,01
	(1)	(5)	(2)	(<1)	(2)	(<1)	(2)	(1)	(1)
HNO_3/HNO_3	0,05	0,05	0,03	0,02	0,02	0,02	0,02	0,00	0,02
	(5)	(5)	(3)	(2)	(2)	(2)	(2)	(<1)	(2)
$HHNO_3$/none	0,05	0,00	0,02	0,00	0,00	0,00	0,01	0,02	0,00
	(5)	(<1)	(2)	(<1)	(<1)	(<1)	(1)	(2)	(<1)
none/HCl	0,05	0,05	0,03	0,00	0,01	0,02	0,02	0,02	0,00
	(5)	(5)	(3)	(<1)	(1)	(2)	(2)	(2)	(<1)
none/HNO_3	0,07	0,05	0,03	0,00	0,02	0,00	0,00	0,02	0,01
	(7)	(5)	(3)	(<1)	(2)	(<1)	(<1)	(2)	(1)
none/none	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
	(<1)	(<1)	(<1)	(<1)	(<1)	(<1)	(<1)	(<1)	(<1)

LEAD

Acid Treatment	Week 0	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8
HCl/HCl	0,14	0,30	0,20	0,26	0,90	0,76	0,37	0,70	0,54
	(1)	(2)	(1)	(1)	(5)	(4)	(2)	(4)	(3)
HCl/none	0,07	0,26	0,10	0,10	0,26	0,29	0,17	0,29	0,11
	(<1)	(1)	(1)	(1)	(1)	(2)	(1)	(2)	(1)
HNO_3/HNO_3	1,17	0,98	0,93	0,61	0,68	0,53	0,54	0,59	0,41
	(6)	(5)	(5)	(3)	(3)	(3)	(3)	(3)	(2)
HNO_3/none	0,11	0,15	0,23	0,32	0,32	0,19	0,20	0,29	0,17
	(1)	(1)	(1)	(2)	(2)	(1)	(1)	(2)	(1)
none/HCl	0,14	0,15	0,07	0,03	0,35	0,12	0,13	0,35	0,07
	(1)	(1)	(<1)	(<1)	(2)	(1)	(1)	(2)	(<1)
none/HNO_3	1,13	0,72	0,93	1,00	0,61	0,47	0,33	0,24	0,22
	(6)	(4)	(5)	(5)	(3)	(2)	(2)	(1)	(1)
none/none	0,14	0,11	0,27	0,06	0,13	0,24	0,13	0,18	0,06
	(1)	(1)	(1)	(<1)	(1)	(1)	(1)	(1)	(<1)

MANGANESE

Acid Treatment	Week 0	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8
HCl/HCl	1,10 (6)	12,50 (63)	10,00 (50)	11,11 (55)	14,89 (75)	11,71 (59)	14,29 (72)	11,10 (55)	6,25 (31)
HCl/none	1,20 (6)	4,17 (21)	3,70 (19)	3,57 (18)	3,85 (19)	3,45 (17)	4,17 (21)	4,00 (20)	5,26 (26)
HNO_3/HNO_3	1,59 (8)	3,13 (16)	4,55 (23)	5,00 (25)	6,67 (33)	7,14 (36)	11,11 (55)	11,11 (55)	14.29 (72)
HNO_3/none	1,10 (6)	1,10 (6)	2,63 (13)	2,38 (12)	2,17 (11)	2,13 (11)	2,78 (14)	2,94 (15)	4,17 (21)
none/HCl	1,30 (7)	1,05 (5)	0,90 (5)	1,00 (5)	2,00 (10)	1,67 (8)	1,41 (7)	1,89 (10)	1,16 (6)
none/HNO_3	0,70 (4)	0,76 (4)	0,80 (4)	2,44 (12)	3,33 (17)	2,78 (14)	4,00 (20)	4,55 (23)	5,00 (25)
none/none	0,60 (3)	0,05 (<1)	0,08 (<1)	0,11 (1)	0,05 (<1)	0,07 (<1)	0,24 (1)	0,40 (2)	0,17 (1)

SILVER

Acid Treatment	Week 0	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8
HCl/HCl	0,03 (0,15)	0,02 (0,10)	0,00 (<0,05)	0,01 0,05	0,02 0,10	0,01 0,05	0,02 0,10	0,02 0,10	0,00 (<0,05)
HCl/none	0,02 (0,10)	0,01 (0,05)	0,00 (<0,05)	0,01 (0,05)	0,02 (0,10)	0,02 (0,10)	0,00 (<0,05)	0,02 (0,10)	0,01 (0,05)
HNO_3/HNO_3	0,06 (0,30)	0,04 (0,20)	0,01 (0,05)	0,00 (<0,05)	0,01 (0,05)	0,01 (0,05)	0,00 (<0,05)	0,01 (0,05)	0,01 (0,05)
HNO_3/none	0,04 (0,20)	0,02 (0,10)	0,00 (<0,05)	0,00 (<0,05)	0,01 (0,05)	0,02 (0,10)	0,02 (<0,05)	0,00 (<0,05)	0,00 (<0,05)
none/HCl	0,01 (0,05)	0,00 (<0,05)	0,00 (<0,05)	0,00 (<0,05)	0,00 (<0,05)	0,01 (0,05)	0,00 (<0,05)	0,01 (0,05)	0,00 (<0,05)
none/HNO_3	0,03 (0,15)	0,01 (0,05)	0,01 (0,05)	0,01 (0,05)	0,00 (<0,05)	0,00 (<0,05)	0,00 (<0,05)	0,02 (0,10)	0,00 (<0,05)
none/none	0,00 (<0,05)	0,00 (<0,05)	0,00 (<0,05)	0,00 (<0,05)	0,00 (<0,05)	0,00 (<0,05)	0,00 (<0,05)	0,00 (<0,05)	0,00 (<0,05)

COPPER

Acid Treatment	Week 0	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8
HCl/HCl	1,00	0,29	0,50	0,14	0,11	0,28	0,36	0,33	0,39
	(5)	(2)	(3)	(1)	(1)	(1)	(2)	(2)	(2)
HCl/none	0,67	0,43	0,13	0,11	0,16	0,28	0,24	0,30	0,11
	(3)	(2)	(1)	(1)	(1)	(1)	(1)	(2)	(1)
HNO$_3$/HNO$_3$	0,67	0,37	0,75	0,43	0,37	0,28	0,36	0,44	0,28
	(3)	(2)	(4)	(2)	(2)	(1)	(2)	(2)	(1)
HNO$_3$/none	1,00	0,21	0,30	0,14	0,16	0,17	0,14	0,44	0,22
	(5)	(1)	(2)	(1)	(1)	(1)	(1)	(2)	(1)
none/HCl	0,33	0,57	0,13	0,14	0,21	0,33	0,14	0,23	0,33
	(2)	(3)	(1)	(1)	(1)	(2)	(1)	(1)	(2)
none/HNO$_3$	0,33	0,57	1,12	0,43	0,58	0,33	0,21	0,44	0,22
	(2)	(3)	(6)	(2)	(3)	(2)	(1)	(2)	(1)
none/none	0,50	0,14	0,13	0,14	0,16	0,17	0,21	0,18	0,28
	(3)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)

COBALT

Acid Treatment	Week 0	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8
HCl/HCl	0,33	0,25	0,44	0,36	0,65	0,60	0,53	0,61	0,50
	(2)	(1)	(2)	(2)	(3)	(3)	(3)	(3)	(3)
HCl/none	0,17	0,08	0,11	0,21	0,29	0,33	0,33	0,39	0,19
	(1)	(<1)	(1)	(1)	(2)	(2)	(2)	(2)	(1)
HNO$_3$/HNO$_3$	0,33	0,45	0,40	0,29	0,29	0,27	0,20	0,28	0,19
	(2)	(2)	(2)	(2)	(2)	(1)	(1)	(1)	(1)
HNO$_3$/none	0,50	0,17	0,22	0,21	0,29	0,20	0,20	0,22	0,25
	(3)	(1)	(1)	(1)	(2)	(1)	(1)	(1)	(1)
none/HCl	0,17	0,08	0,11	0,14	0,29	0,13	0,20	0,28	0,19
	(1)	(<1)	(1)	(1)	(2)	(1)	(1)	(1)	(1)
none/HNO$_3$	0,17	0,33	0,22	0,11	0,24	0,13	0,20	0,22	0,19
	(1)	(2)	(1)	(1)	(1)	(1)	(1)	(1)	(1)
none/none	0,33	0,25	0,11	0,21	0,18	0,20	0,13	0,22	0,13
	(2)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)

URANIUM

Acid Treatment	Concentration after 4 months
HCl/HCl	< about 1 µg/l
HCl/none	< about 1 µg/l
HNO_3/HNO_3	< about 1 µg/l
HNO_3/none	< about 1 µg/l
none/HCl	< about 1 µg/l
none/HNO_3	< about 1 µg/l
none/none	< about 1 µg/l

APPENDIX 3

Duplication of the Uranium Contamination Experiment.

The uranium contamination test described in section 2.33, which showed that uranium was not a potential contaminant, was repeated in order to verify this important result. The (initially U- free) test solutions described in section 2.35 and which contained HCl, HNO_3 and $HClO_4$ were analysed at Pelindaba after 12 weeks of storage. In no instance could U be detected (<about 1μg/1).

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NOTES AND ADDENDA