1-1996

Retention and Separation Behaviour of Chloropyrifos and Other Water Pollutants Using Polyurethane Foams

Rashed Saleh Al-Mehrazi

بسم الله الرحمن الرحيم

UNITED ARAB EMIRATES UNIVERSITY
FACULTY OF SCIENCE

RETENTION AND SEPARATION BEHAVIOUR OF CHLOROPYRIFOS AND OTHER WATER POLLUTANTS USING POLYURETHANE FOAMS

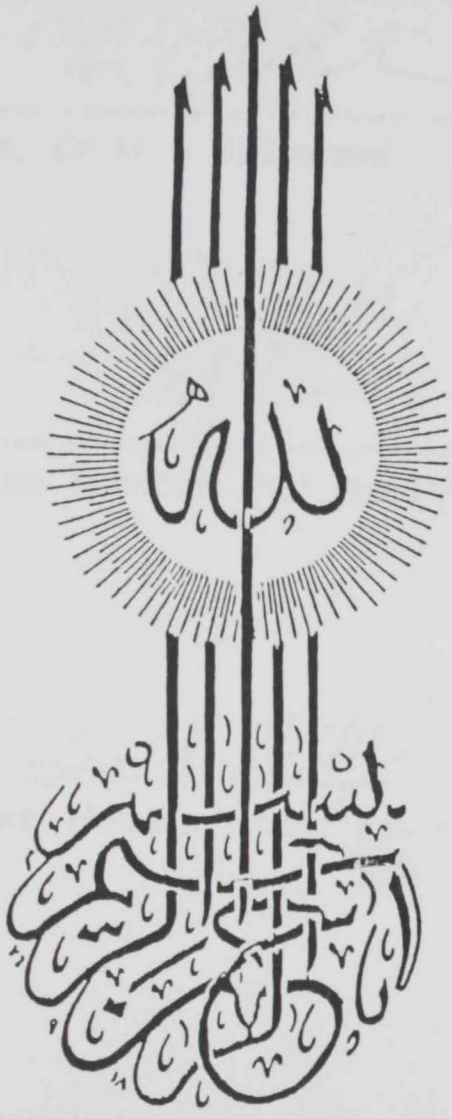
A Thesis

Submitted to the Faculty of Science of the
United Arab Emirates University in Partial Fulfillment of
the Requirements for the Degree of Master of Science
in Environmental Science

By

Rashed Saleh Al-Mehrezi
B.Sc. Major Biology / Minor Chemistry
Chapman College, California (1985)

United Arab Emirates University
Faculty of Science
January 1996



قالوا سبحانك لا علم لنا إلا ما علمتنا

إنك أنت العليم الحكيم

صدق الله العظيم

The thesis of Rashed Saleh Ali Al-Mehrezi for the degree of Master of Science in Environmental Sciences is approved

m. s. el shahawi

.....

Chair of Committee, Dr. M. S. El-Shahawi

Sherif Kandil

.....

Examining Committee Member, Prof. Sherif H. Kandil

Z. M. El Attal

.....

Examining Committee Member, Prof. Zakaria M. El-Attal

.....

Dean of the Faculty of Science, Prof. A. S. Al-Sharhan

United Arab Emirates University

1996

Title : Retention and Separation Behaviour of Chloropyrifos and Other water Pollutants Using Polyurethane Foams.

Name : Rashed Saleh Al-Mehrezi

The thesis of Rashed Saleh Al-Mehrezi for the degree of Master of Science in Environmental Science is approved

Name	Signature
1- Dr. M.S. El-Shahawi Chair of Committee	.....
2- Prof. Sherif H.Kandil Examining Committee Member	.....
3- Prof . Zakaria M.El -Attal Examining Committee Member	.....

Prof . Abdul Rahman S.Al-Sharhan
Dean, Faculty of Science

United Arab Emirates University
Faculty of Science
Department of Chemistry

Title : Retention and Separation Behaviour of Chloropyrifos and Other Water Pollutants Using Polyurethane Foams

Name : Rashed Saleh Al-Mehrezi

Supervisors

Name	Position	Signature
Dr. M.S. El-Shahawi (Supervisor)	Associate Professor Department of Chemistry Faculty of Science United Arab Emirates University	----------
Committee Members		
1. Prof. M.H. Abdel-Kader	Professor of Physical Chemistry National Institute of Laser Research Cairo University Egypt	----------
2. Prof. M.A.Q. Khan	Professor of Biochemistry and Toxins, Michigan University Michigan, United States	----------
3. Dr. S.M. Aldhaheri (Co-Supervisor)	Lecturer of Analytical Chemistry Department of Chemistry Faculty of Science United Arab Emirates University	----------

NOTE

Besides the work carried out in this thesis, the candidate Rashed Saleh Al-Mehrezi pursued postgraduate studies for the partial fulfillment of the M.Sc. degree in Environmental Science in the following topics

A. Core Courses:

Environmental Science I
Environmental Science II
Environmental Law
Social Impact Assessment
Instrumental Analysis

B. Special Courses:

Seminar
Applied Statistics
Environmental Chemistry
Soil and Water Pollution
Environmental Pollution and Pesticides
Food Contamination
Selected Topics in Physical Science
Independent Study on Environmental Science

Prof. Abdul Rahman S. Al-Sharhan
Dean, Faculty of Science

TABLE OF CONTENTS

TABLE OF CONTENTS

CHAPTER 2

Preconcentration and Separation of Some Water Soluble Pyrethroid and Organophosphorous Insecticides on Polyether-Based Polyurethane Foams

Page

CHAPTER 3

Sensitive Detection and Semiquantitative Determination of Bismuth(III) with Some Chromogenic Reagents Immobilized on Polyurethane Foams

CHAPTER 4

ACKNOWLEDGEMENT

ACKNOWLEDGEMENT

The author would like to thank Professor Mohamed K. Yousef, the Deputy Vice Chancellor of the Academic Affairs, U.A.E. University and Professor A.S. Al-Sharhan, Dean of the Faculty of Science, the United Arab Emirates University for their support and encouragement.

Moreover, I wish to express my sincere appreciation to Professor A.M. Kiwan, Head of the Chemistry Department, Faculty of Science, U.A.E. University for providing the facilities and encouragement for this work.

I would like to thank my supervisor Professor M.H. Abdel-Kader, Professor of Physical Chemistry, National Institute of Laser Research, Cairo University for valuable advice throughout my work.

I would like to express my sincere appreciation and gratitude to my supervisor Dr. M.S. El-Shahawi, Associate Professor of Analytical Chemistry, Faculty of Science, U.A.E. University for suggesting the point of research, expert supervision, valuable advice, guidance and patience throughout the experimental work and preparation of the thesis.

I wish to express my sincere appreciation to my supervisor Dr. S.M. Aldhaheri, Lecturer of Analytical Chemistry and the General Director of the Federal Environmental Agency, United Arab Emirates for his interest and encouragement.
I would like also to express my deep gratitude to Professor M.A.Q. Khan, Professor of Biochemistry and Toxins, Michigan University for training me on GC technique.

I would like to express my sincere appreciation to Dr. A. El-Bershamgy and all members in the Central Laboratory at Al-Ain, Ministry of Agriculture and Fisheries.

Special thanks to Mr. M. Shahid for his patience and excellent typing the thesis.
I wish to thank my family for their encouragement and last but not least, I extend my thanks to everyone who gave me the help and advice during the preparation of this work.

A sincere appreciation to Mr. B. Al-Hindawy for his assistance in recording the Infrared Spectra of some of the reagents.

R.S. Al-Mehrezi

ABSTRACT

ABSTRACT

Heavy metals and pesticides represent a class of man-made environmental pollutants which also occur naturally in the environment. The presence of these pollutants in the industrial and agricultural wastewaters often represents a risk to the environment. Investigation of these species in the water is an important aspect of environmental pollution as human activities contributed to the progressive increase in the concentration of these compounds in the environmental as well as aquatic systems. Therefore, identification and removal (or reduction) of these species to an acceptable concentration are of prime importance.

The analytical utility of unloaded open-cell polyurethane foams and foams immobilizing some chromogenic organic reagents (chromoforms) as cellular solid extractor, is considered as a useful addition to the field of separation science and preconcentration techniques. Polyurethane foam allows the isolation of the analyte from the matrix and yields an appropriate enrichment factor. The quasi-spherical membrane structure, the good hydrodynamic and the resilience properties of the foam offers real advantages over the well known granular supports e.g. Voltaleff which is considered one of the excellent support in the literature in separation and preconcentration of trace amounts of organic and inorganic pollutants from different media.

In the present study polyether type polyurethane foam has been used as a trapping medium for the preconcentration and quantitative recovery of some pyrethroid and phosphorous insecticides (commonly in use by the Ministry of Agriculture and Fisheries of UAE) from high volume sample of agricultural waters. The detection and semiquantitative determination of bismuth(III) in aqueous acidic media by polyether foam employing 1,5-di-(phenyl)-3-mercaptoformazan (H_2Dz) and 1,5-di-(2-fluorophenyl)-3-mercaptoformazan (F_2H_2Dz) have been critically investigated.

Unloaded foams were employed in static and dynamic modes for the retention and separation behaviour of a series of pesticides e.g. Cypermethrin, Parathion, Malathion and Chloropyrifos in aqueous media. The effect of different parameters, e.g. contact time, extraction media, solution pH, insecticide concentration, temperature, salt effect and cation size of adding salts affecting the retention behaviour of each insecticide on unloaded foam was investigated. The sorption behaviour of Parathion and Malathion in the presence of different univalent cation sizes increased in the order :

$$Li^+ > Na^+ > K^+ > NH_4^+$$

in good agreement with the solvent extraction mechanism, while Cypermethrin and Chloropyrifos follow the sequence:

$$K^+ > NH_4^+ > Na^+ > Li^+$$

indicating sorption of these species by the "cation chelation mechanism". The thermodynamic parameter, e.g. ΔH° and ΔS° for the sorption process of the tested insecticides by the unloaded foams were obtained. The column performance, the critical capacity, the highest equivalent to the theoretical plates (HETP) and the number of the theoretical plates (N) were also calculated and discussed. Separation of some of the tested insecticides was also achieved.

Plant analysis of Tomato and Parsley plants untreated and sprayed with Chloropyrifos for different time intervals 24, 72 and 120 hrs. was carried out. The analysis of nitrogen, phosphorous, sodium, potassium, copper, zinc, manganese, iron, humidity, wet weight and dry weight of controlled and sprayed plants were achieved and discussed.

The qualitative and semiquantitative determination of bismuth(III) in aqueous acidic (pH < 5) employing the chromogenic reagents H_2Dz- and F_2H_2Dz- immobilized or plasticized tri-n-butylphosphate (TBP) loaded foams were achieved via batch, dynamic and pulsating column modes of extraction.

i) In the batch extraction mode, the detection of 0.02 ppm of bismuth(III) in aqueous acidic solution from a mixture containing the tested metal ion and F_2H_2Dz was achieved on unloaded foams. The detection of 0.01 and 0.005 ppm of bismuth(III) were also obtained with polyurethane foam treated with F_2H_2Dz and

plasticized F_2H_2Dz-TBP foams, respectively. As low as 0.02 ppm of bismuth(III) were also detected on polyurethane foams loaded with H_2Dz or plasticized H_2Dz-TBP foams. The semiquantitiative determination of bismuth(III) in aqueous acidic solution employing polyurethane foam loaded and plasticized with H_2Dz and F_2H_2Dz was successfully carried out.

ii) In the flow (column) technique, the detection and semiquantitative determination of bismuth(III) ions were successfully achieved at the ng cm^{-3} (ppb) concentration level using immobilized and plasticized polyurethane foam with the reagents H_2Dz and F_2H_2Dz. The length of the coloured zone was taken as a semiquantitative measure of metal ion concentrations.

iii) Based on the resilient properties of the open-cell polyurethane foam it was possible to detect as low as 5 ppb of bismuth(III) in aqueous acidic solution by plasticized F_2H_2Dz-TBP foams in pulsating column technique after 25 successive pulses. Semiquantitative determination of bismuth(III) was also possible by this mode of extraction at constant number of pulses.

iv) The selectivity of the proposed F_2H_2Dz-loaded foam on the detection of 1 μg of bismuth(III) in the presence of various interfering ions by batch mode of extraction was critically investigated.

LIST OF FIGURES

List of Figures

LIST OF TABLES

List of Tables

CHAPTER 1
GENERAL INTRODUCTION

1. INTRODUCTION

1.1. Historical Overview:

From the historical point of view, natural sponge is considered to be the oldest application of a solid material of quasi-spherical membrane (foam) geometry in separation chemistry (Braun, *et al.*, 1985). More than four centuries ago (Brunschwig, 1512), a sponge material loaded with olive oil was used for the purification of ethanol in a distillation system (Braun and Farag, 1978). The sponge material can be considered as a solid support, olive oil as a loaded stationary phase, and ethanol vapours as a mobile phase. In 1964, Lal *et al.*, described a method for the preconcentration of trace elements from sea water employing natural sponge supporting iron(III) hydroxide precipitate. The same authors were able to collect silicon, beryllium, gold and titanium by towing the treated foam through sea water.

In 1970, Bowen initiated the application of unloaded polyurethane foams for the sorption and recovery of some selected organic and inorganic components e.g. phenols, iodine, antimony(III) & (V), tin(II) and (IV) and bromine etc. from aqueous solutions containing these species. Based on the pioneering work of Bowen, Gesser *et al.*, 1971 initiated the application of untreated polyurethane foams for the sorption of trace organic contaminants e.g. phthalate esters, organic dyes and pesticides from water. In 1972a, Braun and Farag started the application

of polyurethane foams for the separation purposes, but in a completely different way by taking the advantage of the spherical membrane shaped geometry of polyurethane foams. The same authors were able to use polyurethane foam in column mode for the chemical separation as a substitute solid material for the traditional granular support in extraction chromatographic system. These pioneering studies resulted in several versatile applications of unloaded and loaded foamed polyurethanes (polyether and polyester type) in separation chemistry. (Braun, *et al.*, 1985; Moody and Thomas, 1982 and Alfassi and Wai, 1992).

The most distinctive feature of polyurethane foams as solid sorbents is their membrane structure which differentiates them from all other types and/or solid sorbents in separation chemistry where all are compact (granular) or porous bulky solids. In addition to the above-mentioned aspects polyurethane foam membranes also present another special characteristics. e.g. the good hydrodynamic and aerodynamic properties (Braun *et al.*, 1985). In the majority of chemical separations using solid membranes as stationary phase, the separation of ions and/or molecules is accomplished through the membrane like structure, i.e. the solid membrane is not sorbent but a differentially separating agent (or a transport medium) brought for the separation in between two similar or different phases. On the contrary, with polyurethane foams, the foam membranes act as sorbents, i.e., the ions and/or molecules to be separated or preconcentrated are retained, i.e. sorbed on/or in the

membranes like structure of the foams. The other unique advantage of using solid foam membranes over bulky (porous) solids as sorbents is the diffusion rates of chemical species in membranes which are considerably larger than those in bulky solids (Palagyi and Braun, 1994).

1.2. Fundamental Knowledge of Foamed Polyurethanes:

Several chemical and physical phenomena contribute largely to the properties of the polyurethane foam (Braun, *et al.*, 1985). Flexible and rigid polyurethane foams of open and closed cell structures with a wide range of properties have been prepared and characterized by Braun and Farag, 1978.

1.2.1. Foam Definition:

Polyurethane foam can be defined as plastic materials in which a proportion of solid phase is replaced by a gas in the form of numerous small bubbles (cells) (Thomas, 1965). The gas may be in a continuous phase to give an open cell material or it may be discontinuous to give noncommunicating cells.

1.2.2. Foam Geometry:

Fig. 1.1 shows a typical polyurethane foam in which the bubbles occupy about 97% of the volume. The polyhedral structure is clearly visible, and the polyhedral on the average are quasi-spherical pentagonal dodecahedra (Braun, *et al.*, 1985). The foams can ideally be viewed as more or less regular collections of solid spherical membranes.

Spatially symmetrical packing is usually based on sphere packings in a plane. There are two symmetry types, cubic and hexagonal. In a planar arrangement there is only one way of close packing. In order to obtain the closest packing in the second layer, each sphere of this layer could be interposed between any three spheres of the first layer. In both packing types the first two layer have the same arrangement and packing pattern is different only in the third layer.

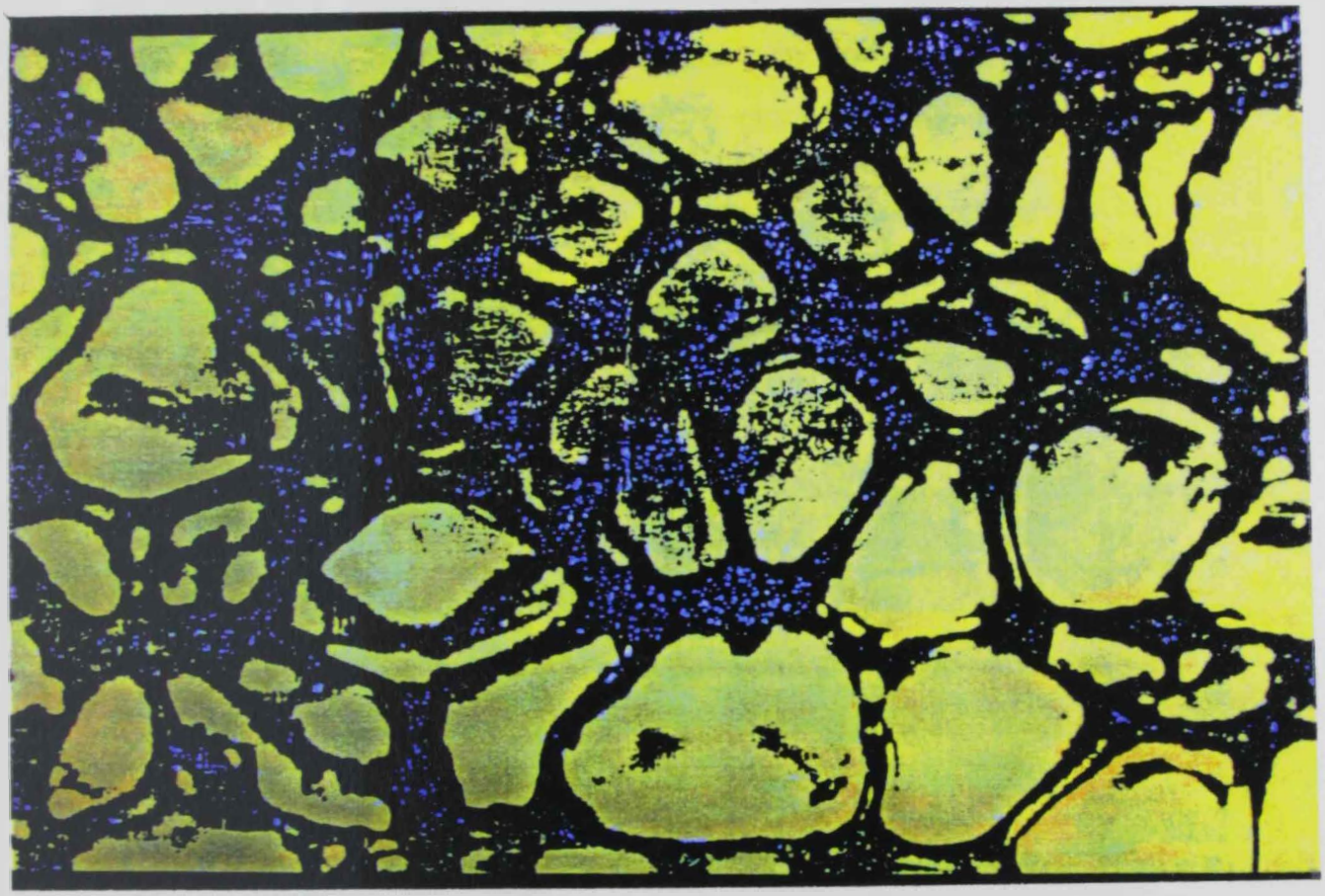


Fig. 1.1. Typical polyurethane foam structure 97% voids

1.2.3. Cell Structure:

The presence or absence of windows (number of windows per cell) in the cell structure is a function of the method of foam preparation (Moody and Thomas, 1982). The same author in 1982 reported that both rigid and flexible polyurethane foams may obtained in closed or open pores cell structure. The structure made up of windowless cells (containing only strands) is named reticulated foam. Closed cell foam can be converted to open-cell foam structure by rupture of the windows mechanically or by applying pressure or chemically by hydrolysis or oxidation (Moody and Thomas, 1982).

1.2.4. Method of Foams Preparation:

The general principle for preparing cellular plastics is dispersion of the gas phase in a liquid phase to obtain liquid foam which will then be solidified to a solid cellular plastic. The main methods for uniform dispersion of the gas bubbles are chemical, physical, or mechanical. The chemical methods include thermal decomposition and blowing by *in situ* chemical reaction (Hunter and Keinfeld, 1965). The former method involves the incorporation of a chemical blowing agent into the plastic polymer in the liquid state. The blowing agent is usually an organic material which decomposes under the action of heat to yield semicarbazide (Hunter and Keinfeld, 1965). This material decomposes

at 235 °C to give nitrogen and carbon dioxide which are useful for expanding plastic such as high density polyethylene and rigid polyvinyl chloride. Blowing by *in situ* chemical reaction involves the formation of gas by a reaction between two species, one of them can or cannot be a part of the polymer, or both from the polymer alone.

Polyurethane foams are the most widely used cellular plastic in separation chemistry (Braun and Farag, 1978a). These foam materials are prepared in soft, flexible or rigid foams and have been fabricated from a variety of polyester and polyether types (Gross, 1969). The two important reactions in the preparation of urethane foams are those between isocyanate and hydroxy compounds (polyester or polyetherpolyols) and those between isocyanate and water. The former reaction for the formation of a urethane group can be considered as a chain propagating reaction in which:

$$R - N = C = O + R - OH \longrightarrow R - [NH - \overset{\overset{O}{\|}}{C} - O] - R \qquad (1.1)$$

Urethane

The second reaction involves the interaction between isocyanate and water is responsible for the foam formation by the liberation of carbon dioxide as an in situ blowing agent as follows:

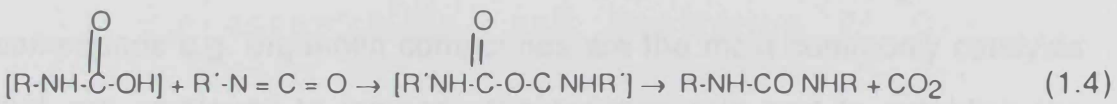
$$R - N = C = O + H_2O \longrightarrow [R - NH - \overset{\overset{O}{\|}}{C} - OH] \longrightarrow R - NH_2 + CO_2 \qquad (1.2)$$

carbamic acid

The first step of the reaction involves the formation of unstable carbamic acid which decomposes to form carbon dioxide and amine. The produced primary amine may react with another isocyanate molecule to form substituted urea as follows:

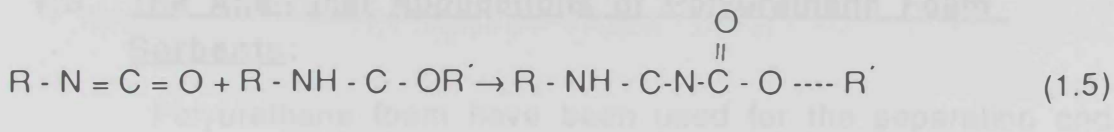
substituted urea (1.3)

On the other hand, carbamic acid may react with another isocyanate molecule to produce carbamic acid anhydride which decomposes to substituted urea and carbon dioxide as shown:

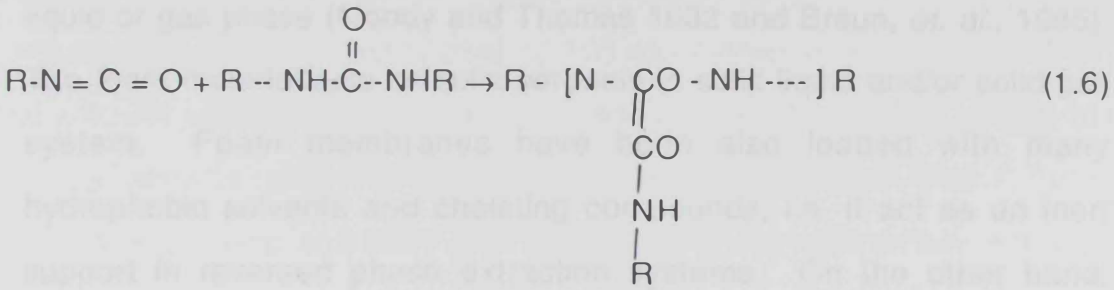


Carbamic acid Carbamic acid anhydride (1.4)

The main reaction which leads to branching and cross-linking polyurethane foams are the isocyanate-urethane reaction producing allophanate linkages and the isocyanate - urea reaction which produce biuret:



Allophanate (1.5)



Biuret (1.6)

The most widely used isocyanate is toluene diisocyanate. The toluene diisocyanates usually employed are the 80/20 and 65/35 mixtures of the 4 and 6 isomers. Tertiary amines and organometallic compounds e.g. organotin compounds are the most commonly catalysts that are employed to increase the reaction rate and to establish the proper balance between the chain extension and the foaming reaction product (David and Staley, 1969).

Generally, physical and chemical properties of Polyurethane foams depend on the method of preparation. The mechanical properties of polyurethane foams are highly dependent on the proportion of the allophanate linkage which increases with reaction time and temperature of toluene diisocyante-based urethanes (Braun and Farag, 1978b).

1.3. The Analytical Applications of Polyurethane Foam Sorbents:

Polyurethane foam have been used for the separation and preconcentration of a wide variety of ionic and non-ionic species from liquid or gas phase (Moody and Thomas 1982 and Braun, *et. al.*, 1985). The foam material acts as solid sorbents in solid-liquid and/or solid-gas system. Foam membranes have been also loaded with many hydrophobic solvents and chelating compounds, i.e. it act as an inert support in reversed phase extraction systems. On the other hand, modified polyurethane foam by chemical anchoring and/or grafting of different chelating agent forming functional groups of the backbone of polyurethane foam have been extensively used in chemical separation (Anjaneyulu *et al.*, 1993).

1.3.1. Preconcentration and Separation of Organic and Inorganic Species with Untreated Polyurethane Foams:

The analytical utility of polyether type polyurethane foams as a solid extractant in the sorption of a number of species from aqueous media was first described by Bowen in 1970. Since then, many studies have been developed for the collection and separation of various organic and inorganic species (Farag *et al.*, 1994). Polyurethane foam has been shown to be a very versatile material for analytical purposes acting as a solid "solvent extractor" in some instances and more complex sorption mechanisms for the extraction of anionic and cationic species were proposed by Palagyi and Braun, 1992.

A thio-substituted polyurethane foam (T-PUF) was developed for use as a selective sorbent for inorganic mercury from complex matrices in industrial effluents (Palagyi and Braun, 1992). The sorption capacity of T-PUF packed columns was superior to other sorbent media and the efficiently of the foam was high at 10-100 ppm levels of Hg from 5-10 dm^3 of effluent volumes. The foam material displayed excellent ability to preconcentrate and recover mercury ions even at low levels from industrial effluents and brine mud generated by the chloroalkali industry (Palagyi and Braun, 1992).

Furthermore, it was reported by Palagyi and Braun, 1994 that heteropoly-molybdates of phosphorus, silicon, arsenic and germanium, both in the reduced and nonreduced forms are effectively sorbed by polyether polyurethane foam. The extraction of gold(III) from aqueous neutral and alkaline cyanide media has also been investigated by polyurethane foam. The unloaded polyurethane foams showed good ability to retain gold-thiourea complex from acidic aqueous solutions (Braun and Farag, 1973b). Schiller and Cook, 1971, examined the separation of gold(III) chloride from natural waters with resilient polyurethane foam sorbent. Gesser and his Co-workers, 1976 have shown that open-cell polyurethane foam of polyether type is an efficient stationary phase in the extraction and recovery of gallium from acidic chloride solutions.

Recently, Carvalho, *et. al.*, 1995, reported the analytical application of polyurethane foam in the direct determination of gallium by X-ray fluorescence. Gallium is determined at levels as low as 60 ng ml^{-1} with a calibration sensitivity of 424 cps. ml/μg within a linear range of 0.1-2.3 $\mu g ml^{-1}$. The procedures were successfully applied for the analysis of gallium in aluminium alloys, bauxite and industrial residue samples (Carvalho, *et. al.*, 1995).

The extraction of antimony(III) and (V) from aqueous hydrochloric acid solution by polyether polyurethane foam has been investigated by LO and Chow 1979. The extraction behaviour of tin(II) and (IV) from acidic chloride media with polyether and polyester foams has been examined (LO and Chow 1981). The sorption behaviour of gold(III), silver(I) and platinum(II) from different halide media by unloaded polyurethane foam has been reported (Koch *et. al.*, 1985). The collection of tantalum(V), antimony(V), and rhenium(VII) from fluoride media has also been investigated. (Caletke *et. al.*, 1985, 1986).

The sorptive capacity of the polyether-based polyurethane foam was determined to be between 0.85 and 0.92 moles/kg for the platinum(II) chloride complex (Schroeder and Chow 1992). In hydrochloric and hydrobromic acid concentrations up to 3.0 M, the platinum(II) bromide complex had higher extraction efficiencies than the platinum(II) chloride complex. The percent of platinum(II) extracted

increased when the alkali metal cations are added in the order $K^+ < Na^+ < Li^+$ for polyether foam and decreased in the order $K^+ > Na^+ > Li^+$ for the polyester foam.

Extraction of alkylammonium tetraphenylborates and dipicrylaminates by polyurethane foam have been studied (Fong and Chow 1992a). Alkylammonium ions are extractable by polyether-and polyester-type polyurethane foams from aqueous solution in the presence of bulky and hydrophobic anions such as tetraphenylborate and dipicrylaminate (Fong and Chow 1992b). The extractability sequences of NH_4^+ > tertiary butylammonium > isopropyl-ammonium > ethylammonium > methyl-ammonium for the extraction with polyether foam and tertbutylammonium almost-equal-to isopropyl-ammonium with polyester foam.

Palagyi and Braun 1992 reported the use of unloaded polyether type polyurethane foams as solid extractants for trace-elements). The membrane properties of the foam sorbents offer unique advantages over conventional bulk type granular sorbents in rapid versatile and effective separations and preconcentrations of different compounds from fluid samples.

The sorption behavior and separation of some metal thiocyanate complexes on polyether-based polyurethane foam have been studied by (Farag *et al.*, 1994). Attempts for the quantitative retention and recovery of the tested thiocyanate complexes by the foam columns were also

made and satisfactory results were obtained. The height equivalent to theoretical plates (HETP) of the foam columns was calculated from the chromatograms and break through capacity curves and it was found to be in the range of 1.8 - 2.3 mm at flow rates up to 15 cm^3/min.

A new method of sorbent supported transport extraction based on the use of open-cell polyurethane foam sorbents in solvent sublation separation has been developed (Palagyi and Braun 1994). The method has shown to be effective for the separation and preconcentration of radioiodine and/or stable iodine from 4 litre of deionized, drinking and surface water using N-cetylpyridinium chloride as a cationic surfactant and nitrogen gas as the bubbling medium.

The sorption of yttrium complexes with 8-hydroxyquinoline and its dihalide derivatives and 8-hydroxyquinoline sulphate by polyurethane foam was critically studied by luminescence and i.r. spectroscopic techniques (Beltyukova, *et al.*, 1995). The spectrophotometric determination of copper and silver as dithizonate complexes on polyurethane foam have been reported by Kundu and Roy, 1992. Beer's law was obeyed over the concentration range 0.05-2.5 μg Cu/ml at 550 nm and 0.01-6.0 μg Ag/ml at 500 nm (Kundu and Roy, 1992).

Polyurethane foam demonstrated to be useful in the separation and concentration of a wide variety of inorganic species from different media (Fong and Chow, 1992c). The extractibility sequences of

$K^+ \simeq Rb^+ > Cs^+ > Na^+ > Li^+$ for the extraction with polyether foam suggested the cation chelation mechanism. The same order of extraction was obtained with polypropylene oxide polyether foam which does not normally adopt a helical structure to form oxygen rich cavities. This indicates that the water - structure enforced ion-pairing (WSEIP) is the driving force for extraction of the ion-pairs (Fong & Chow, 1992d).

In 1992 Stewart and Chow reported the analytical utility of polyurethane foam for the separation of tellurium and selenium by polyurethane foam sorbents. Tellurium is extracted rapidly with > 99% sorbed in 2 min from hydrochloric acid / sodium bromide while selenium was extracted slowly. A method for selective extraction of manganese(II) with dithizone and potassium thiocyanate has been reported by Chakraborti and Roy, 1993. The method involves formation of a Mn(II)-thiocyanate-dithizone complex in a hexamine medium containing potassium thiocyanate, dithizone and hydroxylamine hydrochloride at pH ~ 6.

1.3.2. Collection and Separation of Inorganic Species with Loaded Polyurethane Foams.

Polyurethane foams supporting various organic and/or inorganic compounds, enzymes and ion exchanges have been prepared and successfully employed for the retention and separation purposes (Braun *et al.*, 1985). The analytical utility of polyurethane foams loaded with tri-

n-butyl phosphate (TBP) in batch and column operation modes for the preconcentration and separation of a series of binary mixture of metal ions have been reported by Braun and Farag, 1972 and 1975. Since then several separations and preconcentrations of inorganic species in aqueous media have been examined by the foams supported solvent extractants (Sukiman 1974, Braun and Farag 1973a and Braun *et al.*, 1973). A series of organic solvents e.g. TBP, methyl isobutyl ketone, diethyl ether, isopropyl ether and ethyl acetate have been used to impregnate the foam membranes (Braun, *et al.*, 1985).

Recently, many hydrophobic chelating agents have been physically immobilized by loading on polyurethane foams. The reagent foams produced were successfully employed in several separation and collection processes. These foams combine both the selectivity of the chelating reagent and the advantageous rapidity of kinetic processes between metal ions in aqueous solution and the reagent immobilized in the foam membranes in batch, column and pulsated column modes (El-Shahawi, *et al.*, 1995). Polyurethane foams immobilyzing dithizone have been employed for the quantitative collection of silver(I), mercury(II) and also methyl mercury(II) chloride (Braun and Farag 1974c and Farag *et al.*, 1987).

The collection of cobalt(II) from aqueous solution on plasticized 1-nitrose-2-naphthol foam have been reported by Braun and Farag, 1975b. On the other hand, benzoylacetone-loaded polyurethane foam has been used for the extraction and separation of copper(II) and cadmium(II) (Braun & Farag, 1975d). Plasticized and unplasticized dimethylglyoxime foams have been employed for the preconcentration and separation of nickel(II) (Farag *et al.*, 1982a). Also, tributyl-n-phosphate plasticized benzildioxime and 1,2-cyclohexanedione foams have been utilized for the extraction and separation of nickel (Lee and Halmann, 1980). Polyurethane foam loaded with 1,2-ethanedithiol have been used for the separation and preconcentration of antimony(III) from natural water (Valente and Bowen, 1977).

Depending on the resilient properity of the open cell polyurethane foams. Braun *et al.*, 1985 have applied the pulsating foam column mode for the detection and semiquantitative determination of I^{131} and Hg^{203}. In this type of analysis the colour comparison was made depending on constant number of pulses in a fixed volume of solution. This method was also applied to detect iron(III) with plasticized amine foam in aqueous thiocyanate media (Farag *et al.*, 1982b).

A very attractive and useful application of reagent foams seems to be the sensitive detection and semiquantitative determination of different inorganic species in aqueous media. Qualitative and semiquantitative determination of zinc(II), lead(II), copper(II), cobalt(II), chromium(VI),

nickel(II), iron(III), cadmium(II), mercury(II), tin(II), silver(I), molybdenum(VI) and bismuth(III) have been carried out using several loaded foams. (Braun and Farag 1974a,b; Farag *et al.*, 1981, 1982a,b, 1986, 1987, 1989b and Farag and El-Shahawi, 1990; Hamza *et al.*, 1985 and 1990; and El-Shahawi *et al.*, 1995).

Foams loaded with various extractants, organic ion-exchangers and inorganic precipitates have been proven as a successful applications for different analytical schemes (Braun *et al.*, 1985). Loaded polyurethane foam was applied to collect gold(III) from waste water containing sodium cyanide, silver and some traces of gold per kg barren (Bowen 1970). Different types of polyurethane foams were applied to collect and recover gold from ammonium hydroxide solution (10%) containing potassium cyanide (Braun and Farag 1973c). Comparison between different types of active carbon and polyurethane type on the retention rates of the gold thiourea complex have been carried out (Braun and Farag 1973b).

Open cell polyurethane foam coated with long chain tertiary amines (Adogen) showed to be an effective extractant for uranium in acidic solutions (Gesser and Ahamed, 1990). The coated foam allowed column flow extraction through flow rates but capacity studies indicated that only a fraction line was available for the complexation of the uranium. Interference of some common metal cations indicated that only Co(II) showed a significant adverse effect on the uranium extraction.

1.3.3. Preconcentration and Separation of Organic Species with Loaded and Unloaded Polyurethane Foams:

The concentration of organic pollutants in aqueous media was determined by chromatographic separation on polyurethane foam columns (Farag and El-Shahawi, 1991). The results of preliminary screening tests on the removal of insecticides by the unloaded polyurethane foam indicated that a reasonable percentage of the insecticides was retained on the foam. Therefore attempts were made to extract these compounds from aqueous media using foam columns. Various parameters affecting the retention and separation of these compounds were studied, including temperature, flow-rate, pH, insecticide concentration, shaking time, sample volume and eluting solvent.

The sorption of fifty-nine organic dyes, indicators and stains by polyester and polyether foams was investigated by the use of aqueous solutions and powdered foam materials (Chow *et al.*, 1990). Compositions were made with sorption from 50% methanol solutions for some dyes and also with solvent extractions done with diethyl ether or ethyl acetate for several dyes. TLC plates in water or a mixed solvent mobile phase were compared to the distribution coefficients with foam.

The behaviour of polyurethane foam, Amberlite® XAD-2 and Amberlite® XAD-4 individually or in combination has been studied (Nerin *et al.*, 1993). Standard atmospheres containing different concentration levels of hexachloro-cyclohexane and chlorobenzene isomers were

generated and trapped in absorbent cartridges. The most efficient system for trapping the test gases is the use of two cartridges connected in series, one containing polyurethane foam and the second containing Tenaz GC.

The application of untreated and polyurethane foams treated with TBP in the preconcentration of some phenols from water via static and flow experiments was carried out (El-Shahawi *et al.*, 1994). Batch experiments with the TBP-loaded foams showed a good affinity toward extraction of the tested compounds as compared to the untreated foams. The use of the unloaded and TBP-loaded foams was also employed in column modes for the preconcentration of the phenols used. The extraction efficiency and the recovery of the compounds from the foam material by the column was obtained up to 100%.

The analytical utility of unloaded and polyester-based polyurethane foams with tri-n-octylamine (TOA) in the removal of some phenols from water was carried out (El-Shahawi, 1994). In static mode the TOA-loaded foams showed a good affinity of extraction towards the investigated compounds as compared to the untreated foams. The TOA-loaded foams were employed in column modes for the extraction and recovery of the tested phenols. The retention efficiency and the recovery of the tested compounds from the loaded foam column were up to 98.5%. Sorption of the compounds by the foam were brought by solvent extraction mechanism. Several investigations have been published

describing the application of foam as a collector for separating and concentrating various pesticides, acaricides, phenols, and other organic substances (El-Shahawi and Al-Dhaheri, 1995).

1.3.4. Performance of Polyurethane Foam to Biodegradable and Bioretentive in Biological Waste:

The analytical utility of polyurethane foam in the retention of bacterial growth in three types of synthetic media for process intensification of anaerobic digestion of swine waste was reported by Hill, 1992. The foam material was effective in retaining biocultures. The nylon mesh proved durable but its bioretentive properties were the poorest among the materials tested. Polypropylene felt was the most superior media material, showing good physical durability and bioretentive characteisitics.

A rotating biological contactor (RBC) coupled to polyurethane foam (PUF) as a porous biomass support was evaluated for the biological treatment of soil refinery effluents, COD, ammonia-nitrogen, phenol, hydrocarbon and suspended solids biodegradation (Tyagi *et al.*, 1992). The RBC-PUF bioreactor gave a better performance than a conventional RBC for the biodegradation of these parameters. A higher concentration of active biomass was observed in the RBC-PUF system than with other treatment systems, and COD removal efficiencies of up to 87% were achieved.

AIM OF THE WORK

1.4. AIM OF THE WORK

The great potentialities of open-cell type resilent cellular plastics polyurethane foam membranes lie in their low density, great available surface area, low cost and large scale availability all over the world for many industrial application. The polyurethane foam can be used as sorbents directly or with minor pretreatment.

The compound classes responsible for pollution of potable water resources include polyaromatic hydrocarbons, polychlorinated biphenyls, detergents, phenols and pesticides. The pesticides are toxic agents and are widely and regularly applied over large areas accessible to the public. These compounds are deliberately directed against living organisms and application occurs almost without control (Afghan *et al.*, 1984). Thus, the objective of this study was focused mainly on extending the possibility of using unloaded porous polyether type based polyurethane foams for the preconcentration, separation and recovery of some well known insecticides e.g. Chlorpyrifos, Parathion, Cypermethrin and Malathion which are commonly in use by the farmers in the United Arab Emirates. The study was also carried out to determine weather the extraction of these species takes place by solvent extraction, cation and anion exchange or by other mechanisms.

On the other hand, in view of the significant production and widespread of bismuth and its compounds, some must enter the environment, (rain and river water and soil solutions) and food chain at

low (not detectable) concentrations. Thus significant accumulation of bismuth may occur in marine animal and land and to a lesser extent in land animals including man. The accumulation of bismuth may cause severe toxic effects in kidney, liver, skin and epithelial surfaces in intimate contact with body fluids. Thus, attempts involving the application of polyurethane foam either loaded or unloaded with some selective and sensitive chromogenic reagents e.g. dithizone and 1,5-di-(2-fluorophenyl)-3-mercaptoformazan have been used for the detection and semiquanti-tative determination of bismuth(III) ions in aqueous media using static (batch), dynamic (column) and pulsated squeezing column techniques. The effect of different interfering elements whether they are introduced as organic or inorganic ions are investigated during this work.

This work is of great importance in overcoming many pollution hazards by bringing them to an acceptable concentration and enable us to achieve simple detection, and rapid semiquantitative determinations of some specified pollutants. The membrane properties of the polyurethane foam give unique advantages over conventional sorbents in rapid, versatile and effective separation of the tested compounds.

CHAPTER 2

PRECONCENTRATION AND SEPARATION OF SOME WATER SOLUBLE PYRETHROID AND ORGANOPHOSPHOROUS INSECTICIDES ON POLYETHER-BASED POLYURETHANE FOAMS

2.1. INTRODUCTION

The insecticides can enter water from various sources. Edward, 1973a,b has reported sources of insecticides to include run-off from agricultural land, direct entry from crop spraying, industrial and sewage effluent, cattle spraying, dust and rainfall. The presence of these compounds in the aquatic environment has been known to cause severe health problems to animals, birds and humans (Chan *et al.*, 1982). The dynamic movement of the pesticides in the aquatic environment is given in Fig. 2.1.

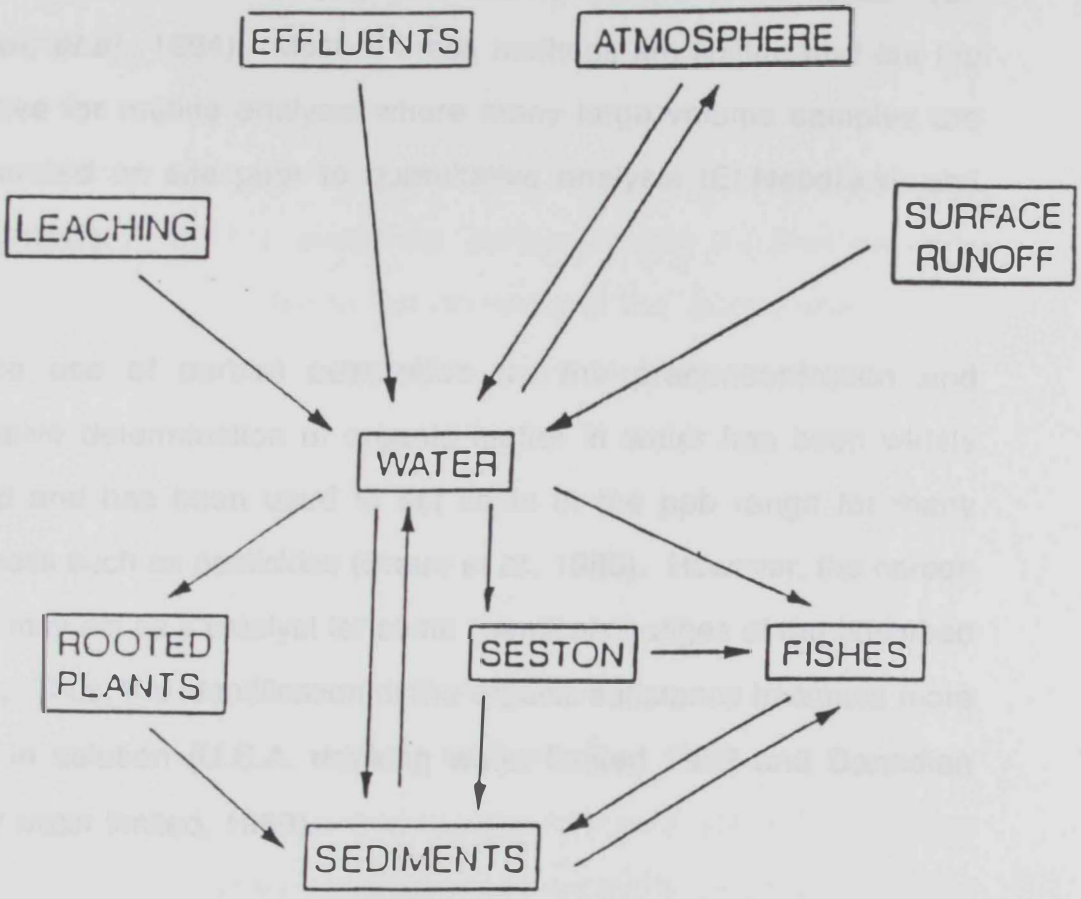


Fig. 2.1: The dynamic movement of the pesticides in the aquatic environment.

The complete removal or reduction of the organic pollutants e.g. pesticides to an acceptable concentration has become a major concern. The most common reported extraction procedures are steam distillation, liquid-liquid extraction, oxidation reactions, reversed phase liquid-liquid partition filter chromatography and adsorption on active carbon (El-Shahawi, *et al.*, 1994). Most of these methods are limited and are too expensive for routine analysis where many large volume samples are concentrated on site prior to quantitative analysis (El-Nabarawy and Bolous, 1987).

The use of carbon adsorption for the preconcentration and quantitative determination of organic matter in water has been widely adopted and has been used to set limits in the ppb range for many substances such as pesticides (Braun *et al.*, 1985). However, the carbon surface may act as a catalyst for some chemical changes of the adsorbed species. Thus, the identification of the organic substance becomes more difficult in solution (U.S.A. drinking water limited 1962 and Canadian drinking water limited, 1969).

Special synthetic resins and C_{18} Corasil have been used for concentrating extremely low levels of polynuclear aromatic hydrocarbons prior to their quantitative analysis (Navratil et al., 1977 and Oylet, *et al.*, 1978). Various methods of adsorption and oxidation reactions have

been reviewed for the removal, separation and identification of phenol and phenol-like compounds in the waste water (Braun *et al.*, 1985).

The use of polyurethane foams in separation and preconcentration processes dates back to Bowen's classical paper (Palagyi and Braun, 1992). These organic compounds are present in water as parts per billion and parts per trillion. Therefore, efficient collection and preconcentration methods are inevitably required to provide enough material for a reliable analytical determination (El-Shahawi and Aldhaheri, 1995) . This led to the revealing of the potentialities of the special geometrical form: quasi membrane-shaped geometry of polyurethane foam as a substitute for the traditional granular supports in extraction chromatography.

Gesser *et al.*, 1971 initiated the application of unloaded foam as culture tube stoppers for the extraction and recovery of some organic pollutants from water at various concentration. Since then several investigations have been reported the application of polyurethane foam plugs for the quantitative extraction and recovery of polychlorinated biphenyls, dieldrin and some DDTs from industrial and agricultural waters have been reported by Braun and Farag, 1978b. The retention and recovery of some phthalate esters from water and air in high volume samples by unloaded polyurethane foam have been carried out (Lewis, *et al.*, 1979).

In recent years, considerable work has been done on the extraction of some organic pollutants by unloaded polyurethane foam from aqueous, non-aqueous and gaseous media (Farag and El-Shahawi, 1991and Fong and Chow, 1992c,d). The results on the removal of some water soluble insecticides by the unloaded polyurethane foam indicated that a reasonable percentage of the insecticides was retained on the foam (Farag and El-Shahawi, 1991). The method can be used to preconcentrate insecticides in tap water and modified to determine dissolved insecticides in industrial and natural waters.

The use of the unloaded, tri-n-octylamine and tri-n-butylphosphate (TBP) loaded foams was employed in column modes for the preconcentration of some phenols and some water soluble acaricides (El-Shahawi *et al.*, 1994 and 1995). The extraction efficiency and the recovery percentage of the phenolic compounds by the foam column were obtained up to 100%. The sorption of the compounds by the foam was brought by a solvent extraction mechanism. The pKa and the molecular weight of the absorbates play an important role in the sorption process.

The goal of the work presented in this chapter is to investigate the analytical utility of open-cell polyether type based polyurethane foam for the quantitative collection and removal of some pyrethroid and organophosphorous insecticides from high volume water samples. These compounds were chosen because they are quite hydrophobic

and are likely to be extracted by the foam. The objective of the study was also aimed to determine whether the extraction takes place by solvent extraction, cation chelation and anion exchange mechanism or by any other mechanisms.

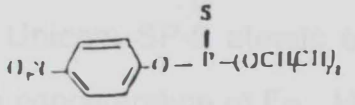
2.2. EXPERIMENTAL

2.2.1. Reagents and Materials:

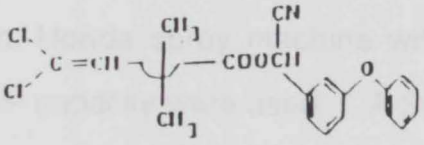
All chemicals used were of analytical reagents grade. Open pores polyether type based polyurethane foam, was supplied by K.G. Schaum (Stoffwerk, Kremsmunster, Austria). Foam cubes of approximately 1 cm^3 were cut from polyurethane foam sheet. The foam cubes were then soaked in 1 M hydrochloric acid for 24 hrs and washed with distilled water until they were acid free. The foam cubes were then washed with acetone in a Soxhlet extractor for 6 hrs (El-Shahawi, 1994). Stock solutions (1M) of lithium, sodium, ammonium and potassium chlorides were prepared separately in distilled water. A Brilton-Robinson buffer (pH 2-12) solutions were prepared by mixing equimolar concentrations (0.08 M) of boric, acetic and phosphoric acids in distilled water and adjusting the pH with sodium hydroxide (0.1M).

The tested insecticides were Parathion, 0,0-diethyl-4-nitrophenyl phosphorothioate(I); Cypermethrin, cyano(3-phenoxyphenyl)methyl 3-(2,2-dichloroethyl)-2,2-dimethylcyclopropanecarboxylate(II); Chloropyrifos, 0,0-diethyl-o-(3,5,6-trichloro-2-pyridyl)phosphorothioate(III) and Malathion, diethyl[(dimethoxyphosphinothioyl)thio]butanedioate(IV). The structure of the tested pyrethroid and organophosphorous is given in Fig. 2.2.

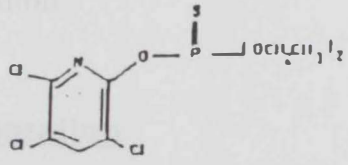
A stock solution of each compound (200 μg/cm^3) was prepared in 100 cm^3 measuring flask by dissolving the exact weight of the compound in distilled and/or tap water (as a natural water resource) in the presence of few drops of ethanol whenever is required. Standard solutions of these compounds were prepared by diluting their stock solutions with distilled or tap water. The solutions were stored in polyethylene bottles (250 cm^3 capacity).



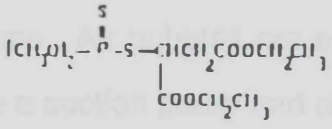
Parathion



Cypermethrin



Chloropyrifos



Malathion

Fig. 2.2. The structure of the tested pyrethroid and the organophosphorous insecticides.

2.2.2. Apparatus

UV absorbance measurements for the determination of the tested insecticides were obtained with a Pye Unicam UV-visible SP8-400 spectrophotometer with 0.2 and 1 cm quartz cells. An O rion pH meter and glass columns (15 cm height x 15 mm I.D.) and Lab-Line Orbit Environ-Shaker model 35271-1 were also used. Corning Flame photometer -410 was used for measuring the concentration of sodium and potassium. A Pye Unicam SP-9 atomic absorption spectrometer was used to measure the concentration of Fe., Mn., Zn. and Cu. Calcium was determined by EDTA titration. Kjeldahl method was used for the determination of the nitrogen content in plant (tomato and parsley) tissues. Hot Box oven, Honda spray machine with high pressure and stoppered flasks, 50 cm^3 capacity were used. A Soxhlet extractor and a rotary evaporator were used for the recovery and analysis of the tested insecticides from the foam column.

2.2.3. Foam Column Preparation

1 g dry foam was packed in a glass column (Fig. 2.3) by applying gentle pressure with a glass rod to reduce the foam volume to about one-third of its original volume. Air bubbles are expelled during packing step by connecting tap (1) to a suction pump and closing tap (2). After about 5 min. of evacuation, distilled water is allowed to fill the column gradually through tap (2) and tap (1) stopper is then replaced with a separating funnel as reservoir.

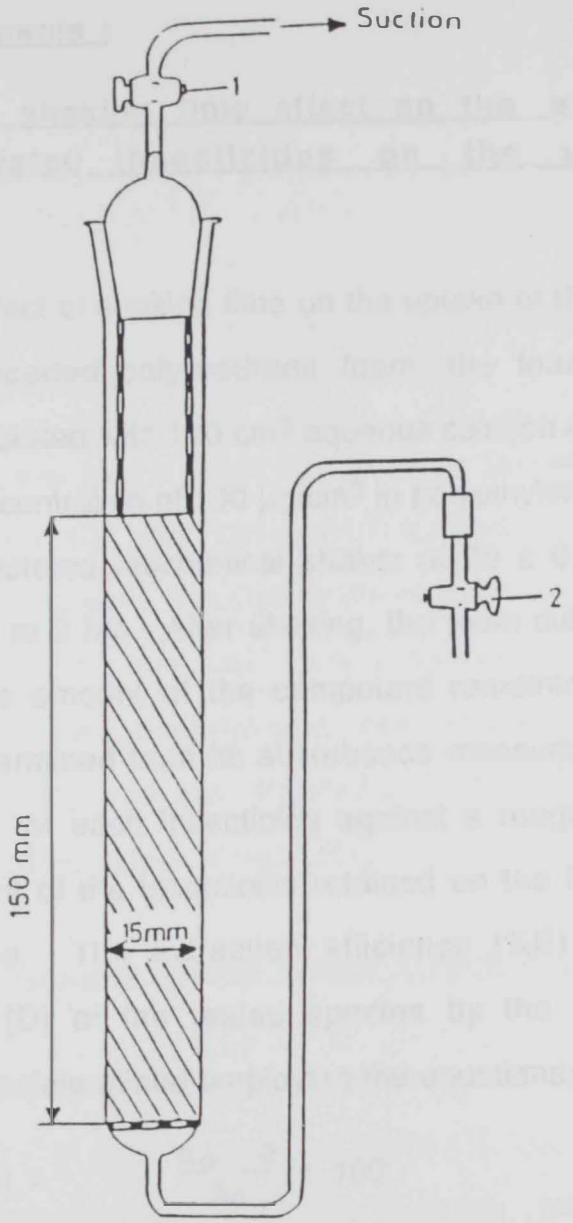


Fig. 2.3: Foam chromatographic column in packing step.

2.2.4. General Procedures:

2.2.4.1. *Batch Experiments* :

2.2.4.1.1 Testing the shaking time effect on the extraction efficiency of the tested insecticides on the unloaded polyurethane foam:

To examine the effect of shaking time on the uptake of the tested compounds, on the unloaded polyurethane foam, the foam cubes (0.3+0.004 g) were equilibrated with 100 cm^3 aqueous solution at pH 5-6 of each compound at concentration of 100 $\mu g/cm^3$ in polyethylene bottles and shaked in a thermostated mechanical shaker at 20 ± 0.1 °C for various time intervals up to 2 hrs. After shaking, the foam cubes were then separated out. The amount of the compound remaining in the aqueous phase was determined from its absorbance measurements at the suitable wavelength for each insecticide against a reagent blank (Table 2.1). The amount of the insecticide retained on the foam was calculated by difference. The extraction efficiency (%E) and the distribution coefficient (D) of the tested species by the unloaded polyurethane foams were determined employing the equations:

$$\%\text{Extraction (E)} = \frac{a_o - a}{a_o} \times 100 \qquad (2.1)$$

where

a_o = Concentration of the tested compound in solution before extraction,

a = Concentration of the solute in solution after extraction,

$$D = \left(\frac{\%\ \text{Extraction}}{100 - \%\ \text{Extraction}}\right) \times \frac{\text{Volume of solution (L)}}{\text{Weight of foam (Kg)}} \qquad (2.2)$$

or

$$D = \left(\frac{\%\ \text{Extraction}}{100 - \%\ \text{Extraction}}\right) \times \frac{\text{Volume of solution (cm}^3\text{)}}{\text{Weight of foam (g)}} \qquad (2.3)$$

2.2.4.1.2. Influence of pH on the extraction of the tested insecticides on the unloaded polyurethane foam:

In 250 cm^3 conical flasks 0.3±0.004 g of the unloaded foam cubes were equilibrated with 100 cm^3 (100 $\mu g/cm^3$) for each of the tested insecticides. These solutions were adjusted to the required pH (2-11) by 20 cm^3 of Britton-Robinson buffers and were shaken for 2 hrs. in a mechanical shaker. The foam material was then separated and the percentage extraction (%E) and the distribution ratio (D) of each insecticide were calculated as before at each pH.

2.2.4.1.3. Sorption isotherm of the tested insecticides on the unloaded foam:

In separate batch experiments 0.3 ± 0.004 g of dry foam cubes were shaken with 100 cm^3 of different concentrations (10-100 $\mu g/cm^3$) of each insecticide at the optimum pH of each one for 2 hrs. After shaking the foam material was separated out and the amount of each insecticide remained in the aqueous solution was measured spectrophotometrically and the amount retained on the foam was calculated by difference.

2.2.4.1.4. Effect of temperature on the extraction percentage of the insecticides on the unloaded foam:

In order to investigate the effect of temperature on the extraction efficiency of each insecticide by polyurethane foam, 0.3 ± 0.004 g dry foam was mixed with 100 cm^3 (100 $\mu g/cm^3$) of each insecticide at the optimum pH in stoppered Pyrex conical flasks at 25, 35, 45 and 55 ± 0.1 °C. After shaking for 2 hrs. the foam material was separated out and the amount of the insecticide remained in the aqueous solution was measured and the amount retained on the foam was calculated by difference.

2.2.4.1.5. Effect of ionic strength on the extraction of the insecticides on the untreated polyurethane foam:

In batch experiments, the influence of various concentration of alkali metal (Li^+, Na^+, K^+ and NH_4^+) chlorides on the sorption profiles of the tested species at 100 $\mu g/cm^3$ by the unloaded foam was carried out. In these experiments 100 cm^3 of each insecticide were mixed with 0.3 ± 0.004 g unloaded foam at $4 < pH < 7$. To these solutions, various concentrations (≤ 0.10 M) of lithium chloride were added and the solutions were shaken for 2 hrs in stoppered flasks. The sorption behaviour of the tested compounds on the unloaded foam was evaluated from the percentage extraction (%E) and the distribution ratio (D). Following these procedures, the effect of NaCl, KCl and NH_4Cl on the sorption profiles of the tested insecticides on the untreated foam were also carried out.

2.2.4.1.6. Influence of the extraction media on the sorption profiles of the tested insecticides on the unloaded foam:

The effect of various concentrations of ethanol on the sorption profiles of the tested species was critically studied in static mode of extraction. In these experiments 100 cm^3 of each insecticide (100 $\mu g/cm^3$) containing ethanol (0-15%) were mixed with 0.3 ± 0.004 g of dry foam. The solutions were then shaken for 2 hrs. and the foam materials were separated out by decantation and the sorption profiles of each insecticide were obtained from the values of % E and D at each ethanol concentration.

2.2.4.2. *Column Experiments* :

2.2.4.2.1. Chromatographic behaviour of the tested insecticides on a column packed with unloaded foam:

Quantitative retention and elution of the tested compounds on the unloaded polyurethane foam columns were carried out using the vacuum method of foam packing (Braun *et al.*, 1985). Tap or distilled water (0.1 dm^3) sample containing 0.1 mg of the tested compound at $5 < pH < 7$ was percolated through the column packed with 1 ± 0.006 g of the unloaded foam at 10 cm^3/min. After squeezing water from the foam material, the compound was then recovered from the foam with 100 cm^3 acetone in a Soxhlet extractor for 6 hrs. The sample quantity was then determined by measuring the absorbance of the extracted acetone solution against a blank reagent after being concentrated to 25 cm^3 with

a rotary evaporator. The effect of sample volume (0.1-6 dm^3) and flow rate (2-25 cm^3/min) on the extraction efficiency of the compounds by the foams were also examined.

Elution of some of the tested insecticides were quantitatively carried out by percolating selective eluting agents of either aqueous solution adjusted at specific pH or by HCl - acetone (1:1 v/v). The elution of Chloropyrifos was carried out efficiently by acetone with an aqueous acidic solution adjusted to pH 2.4. Measurement of the effluent concentration was carried out spectrophotometrically for each insecticide at λ_{max} (Table 2.1).

2.2.4.2.2. Capacity :

Break-through capacity was defined as the amount of the tested compound that could be retained on the column when the insecticide was allowed to pass through the column at a reasonable flow rate ($\leq$ 5 cm^3 min^{-1}) until the insecticide was first detected in the effluent solution. A solution of 50 μg cm^{-3} of each insecticide in tap (or distilled) water was used at the optimum pH of each compound. The solution of each compound was percolated through the foam column packed with 1 $\pm$ 0.006 g of the unloaded foam at a flow rate of 5 cm^3/min until the effluent solution concentration reached that of the feed one. The measurement of the effluent concentration of the tested species were carried out as before.

2.2.5. Plant Analysis:

2.2.5.1. Sample preparation:

Plant sample (leaves) of Tomato and Parsley were sprayed with 20 g of commercial Chloropyrifos (40% w/w) mixed with 20 dm^3 water ($4{:}1x10^4$ w/v) in the open field using high pressure sprayer. The plant samples were left for a period of 24, 72 and 120 hrs. Two samples of each controlled and treated leaves were then collected, washed with distilled water until all dust and sand removed completely and finally dried with napkin. The leaves were cut into small pieces, washed with water and spread for 24 hrs. in room temperature for drying and then ground in powder form (Chapman and Pratt, 1961).

2.2.5.2. Determination of the total nitrogen content:

Weigh an accurately weight of the dry leave (0.2 - 0.3 g) and place it in 800 cm^3 Kjeldahl flask and add 50 cm^3 of concentrated sulphuric acid containing 1.65 g of salicylic acid. Add 5 gm of sodium thiosulphate, heat for 30 min, cool and then add 10 g of sodium hydrogen sulphate - selenium mixture (100:1 w/w) and digest in Kjeldahl apparatus. After complete digestion, cool and add 300 cm^3 water and 100 cm^3 of concentrated sodium hydroxide. Distill and titrate the distillate with standard sulphuric acid. Determine the percentage of the nitrogen content employing the equation:

$$\%\,N = \frac{N.V \times 14}{10 \times w} \qquad (2.4)$$

where N and V are the normality and volume in cm^3 of sulphuric acid consumed in the titration and w is the weight of the dry leaves in grams.

2.2.5.3. Determination of P, Na, K, Cu, Zn, Mn and Fe by wet ashing:

Place an accurately weight (2-3 g) of the grinded plant material in 250 cm^3 beaker and add 20 cm^3 of concentrated sulphuric-perchloric acid mixture (1:1 v/v). Heat the reaction mixture on a hot plate until the acid fumes are completely evolved. Reduce the volume of the reaction mixture to 3-5 cm^3 by evaporation on a hot plate and add 50 cm^3 of distilled water to dissolve the residue. Transfer the solution to 100 cm^3 volumetric flask and complete with distilled water to the mark. Construct calibration graphs for phosphorous by UV-visible spectrophotometry with molybdate; sodium and potassium by flame photometry and copper, zinc, manganese and iron by atomic absorption spectrometry. The unkown sample concentration is then obtained from a calibration graph of each element employing the following equation:

$$\% M = \frac{C(ppm) \times \text{solution volume } (cm^3)}{10^4 \times \text{sample weight (g)}} \qquad (2.5)$$

where M = P, Na, K, Cu, Zn, Mn or Fe and C is the concentration of the element to be determined in ppm.

2.2.5.4. Determination of moisture or humidity content

Spread the sample in the container and weigh rapidly. Dry in an air-circulation oven at 70-80 °C to a constant weight. Cool in a desiccator, weigh and find the humidity and dry matter percentages employing the equations.

$$\text{Moisture (\%)} = \frac{\text{Loss in weight on drying (g)}}{\text{initial sample weight (g)}} \times 100 \quad (2.6)$$

$$\text{Dry matter (\%)} = \frac{\text{Oven dry weight (g)}}{\text{initial sample weight (g)}} \times 100 \quad (2.7)$$

2.2.5.5. Ash Content

Preheat a crucible in a muffle furnace to about 500 °C. Cool in a desiccator and weigh. Transfer an accurately weight 1 g of oven-dried sample in the crucible. Place the crucible containing the dry sample in a R.T. muffle furnace and allow the temperature to rise to 500 °C. After 3 hrs. at 500 °C remove the crucible, allow it to cool in a desiccator and weight. Determine the ash content employing the equation:

$$\text{Ash (\%)} = \frac{\text{ash weight (g)}}{\text{oven dry weight (g)}} \times 100 \quad (2.8)$$

2.2.5.6. Dry Ashing

Weigh 0.2 g air-dried of grinding sample into an acid-washed porcelain basin. Ignite to 500 °C for 3 hrs. in a muffle furnace (refer to ashing procedure). Cool, add 5 cm^3 of HCl (1:1 v/v) then cover with a watch glass and heat on a steam bath for 15 mins. Add 1 cm^3 of concentrated HNO_3, evaporate to dryness and continue heating for 1 hr. to dehydrate silica. Add 2 cm^3 HCl (1:1 v/v), swirl to dissolve the residue then dilute to 20 cm^3 with water and warm to complete dissolution. Filter through a No. 44 filter paper into 100 cm^3 volumetric flask and dilute with distilled water to the mark. Carry out blank determination in the same way (Chapman and Pratt, 1961).

2.3. RESULTS AND DISCUSSIONS

The use of unloaded polyurethane foams (PUF) in separation and preconcentration processes led to the revealing of the potentialities of their spherical geometrical form: spherical membrane-shaped geometry and to the proposal of their general use in column operations as a substitute for the traditional granular supports in extraction chromatography. The membrane like structure of the foams together with the efficient sorption and mass-transfer properties offer higher concentrating ability and flow rate compared with other solid supports. The solid foam concentrates various species in solution by a phase distribution mechanism rather than adsorption. Thus, in recent years considerable progress has been made in the use of polyurethane foam as an inexpensive solid extractor and effective sorbent for the removal of water pollutants.

2.3.1. Retention behaviour of the tested compounds on unloaded foams by batch experiments:

Batch experiments using unloaded polyurethane foam have shown that, the extraction of investigated insecticides Parathion(I), Cypermethrin(II), Chloropyrifos(III) and Malathion(IV) is rapid and the equilibrium is reached in less than 50 min., followed by a plateau. Hence a minimum 1 hr. shaking time was adopted in the subsequent work. The results obtained are summarized in Fig. 2.4. A good extraction performance and rapid preconcentration of the tested compounds from aqueous media were obtained. The average values of the half-life ($t_{1/2}$) of equilibrium sorption calculated from Fig. 2.4 were

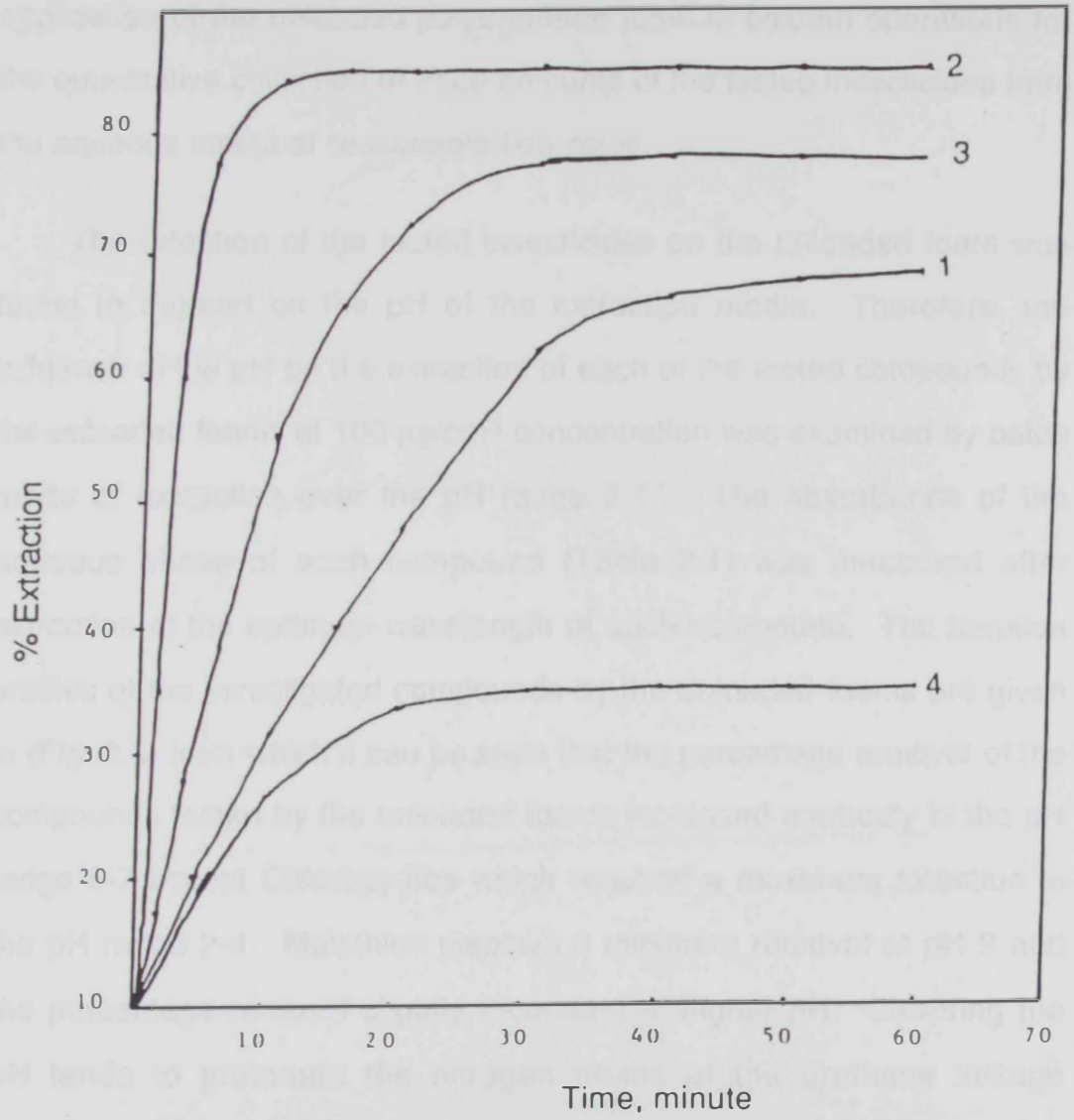


Fig. 2.4. Effect of shaking time on the sorption profiles of Parathion (1), Cypermethrin (2), Chloropyrifos (3) and Malathion (4) at 100 mg/cm^3 in aqueous solution (100 cm^3) at pH 5-7 and 20 ± 0.1 °C by unloaded foam (0.3 ± 0.004 g).

found in the range 2-3 mins. These results suggest the possible application of the unloaded polyurethane foam in column operations for the quantitative collection of trace amounts of the tested insecticides from the aqueous media at reasonable flow rates.

The retention of the tested insecticides on the unloaded foam was found to depend on the pH of the extraction media. Therefore, the influence of the pH on the extraction of each of the tested compounds by the unloaded foams at 100 $\mu g/cm^3$ concentration was examined by batch mode of extraction over the pH range 2-11. The absorbance of the aqueous phase of each compound (Table 2.1) was measured after extraction at the optimum wavelength of each compound. The sorption profiles of the investigated compounds by the unloaded foams are given in (Fig. 2.5) from which it can be seen that the percentage removal of the compounds tested by the unloaded foams increased markedly in the pH range 5-7 except Chloropyrifos which reached a maximum retention in the pH range 2-4. Malathion displays a minimum removal at pH 9 and the percentage removal slightly increased at higher pH. Lowering the pH tends to protonate the nitrogen atoms of the urethane linkage (a) and/or the ether oxygen (b) atoms of the polyurethane foam (El-Shahawi, 1994) as follows :

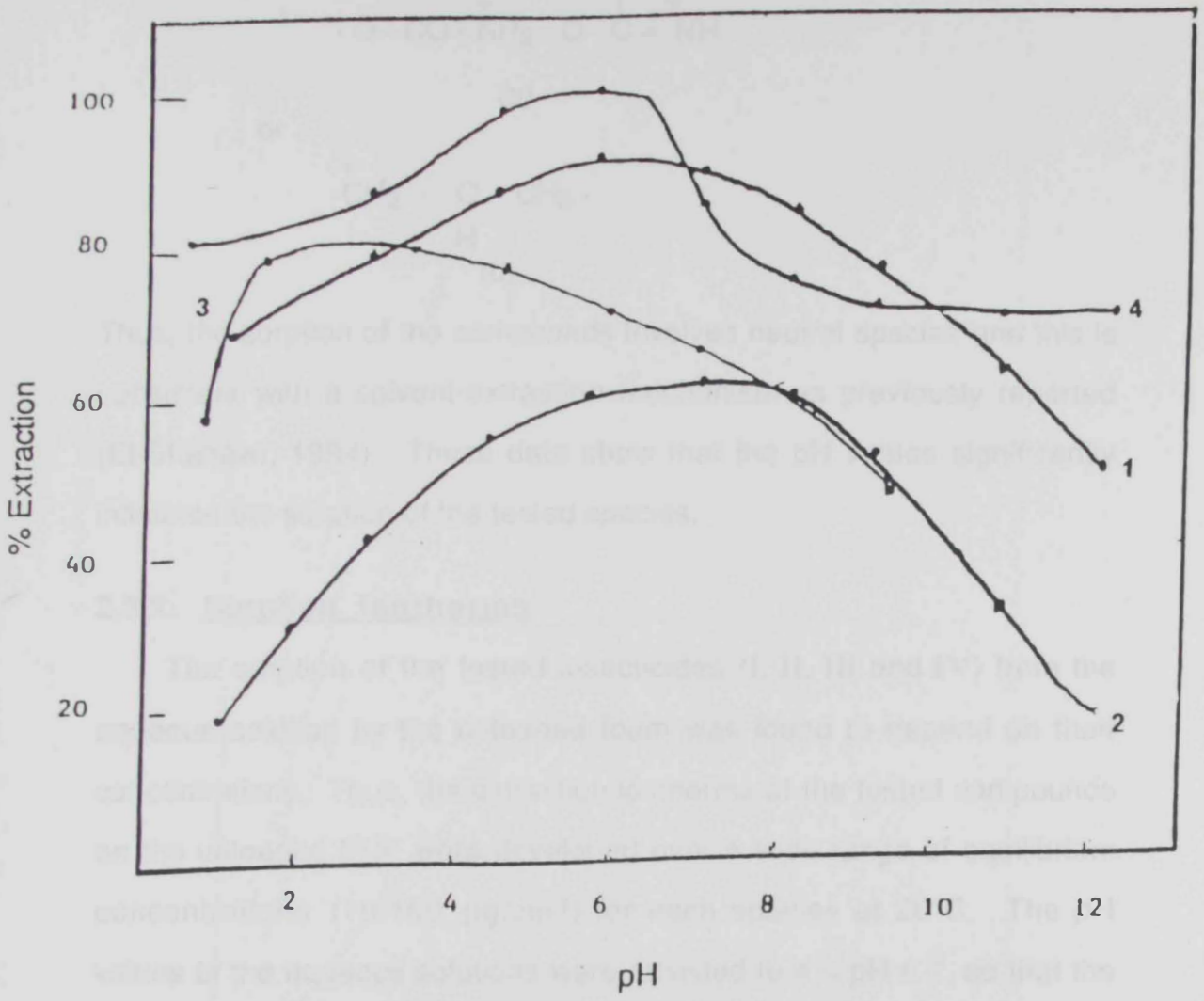
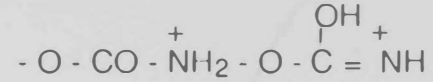
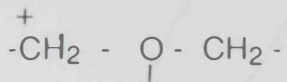


Fig. 2.5. Effect of pH on the extraction percentage of Parathion (1), Cypermethrin (2), Chloropyrifos (3) and Malathion (4) at 100 mg/cm^3 by unloaded foam (0.3 ± 0.004 g) from 100 cm^3 aqueous sample. Other extractions as in Fig. 2.4 and 1 hr. extraction time.



(a)

or



(b)

Thus, the sorption of the compounds involves neutral species and this is consistent with a solvent-extraction mechanism as previously reported (El-Shahawi, 1994). These data show that the pH values significantly influence the sorption of the tested species.

2.3.2. Sorption Isotherms

The sorption of the tested insecticides (I, II, III and IV) from the aqueous solution by the unloaded foam was found to depend on their concentrations. Thus, the extraction isotherms of the tested compounds on the unloaded PUF were developed over a wide range of equilibrium concentrations (10-100 $\mu g/cm^3$) for each species at 20°C. The pH values of the aqueous solutions were adjusted to $4 \leq pH \leq 7$, so that the compounds were predominately in the undissociated form. At low concentration of the compounds, the sorption isotherms exhibited a first order behaviour (good linear relationship) and tended to plateau at higher bulk solution concentration. Fig. 2.6 shows plots of the remaining concentration of the tested insecticides in the aqueous phase versus their concentration retained on the foam material. The sorption of the different species by the unloaded foam increases in the order:

Cypermethrin > Chloropyrifos > Parathion > Malathion (2.9)

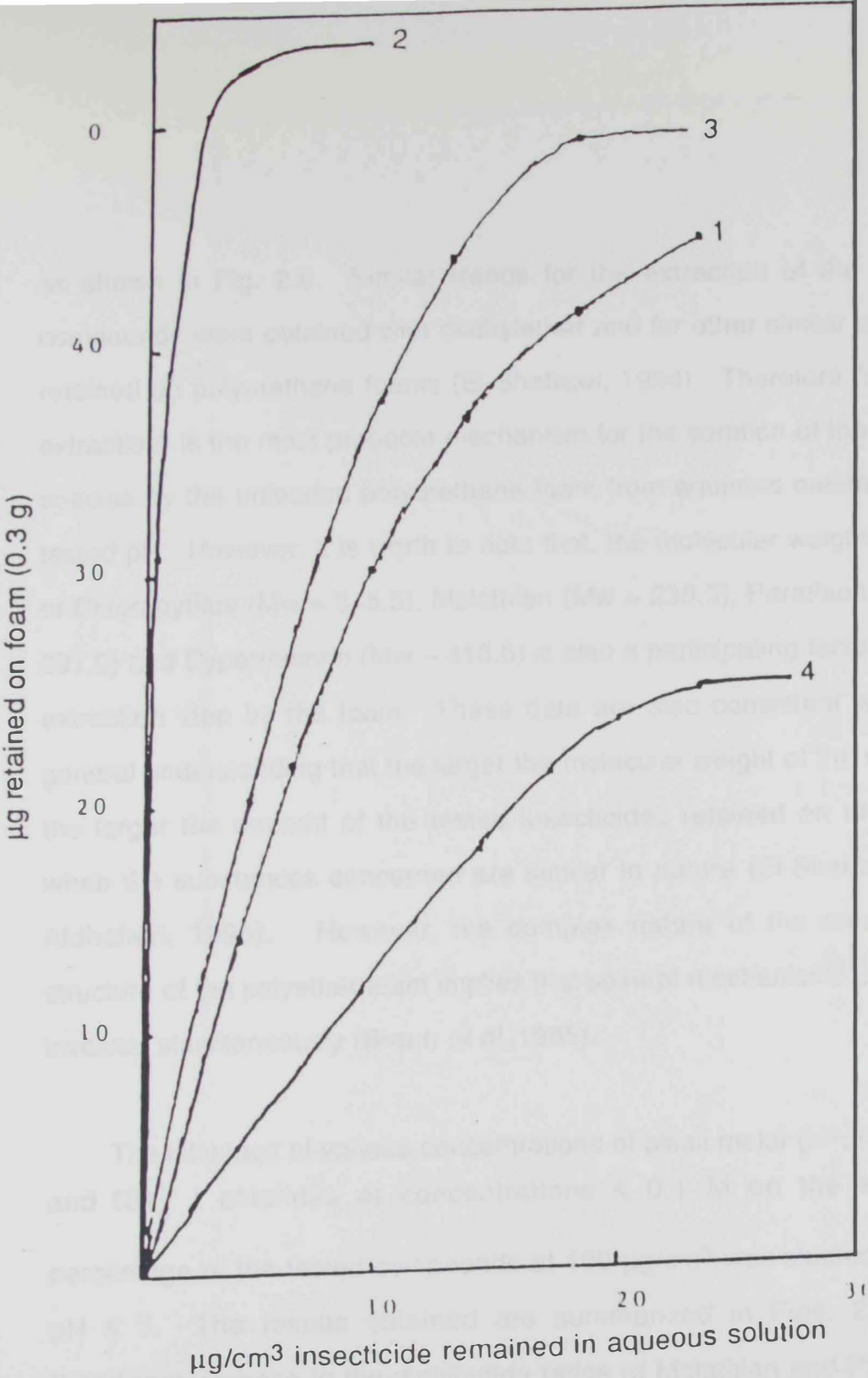


Fig. 2.6. Extraction isotherm of Parathion (1), Cypermethrin (2), Chloropyrifos (3) and Malathion (4) at concentration 100 mg/cm^3 by unloaded foam (0.3 ± 0.004 g) from 100 cm^3 aqueous sample at 4-7 and 20±0.1 °C and 1 hr. extraction time.

as shown in Fig. 2.6. Similar trends for the extraction of the tested compounds were obtained with diethylether and for other similar species retained on polyurethane foams (El-Shahawi, 1994). Therefore "solvent extraction" is the most probable mechanism for the sorption of the tested species by the unloaded polyurethane foam from aqueous media at the tested pH. However, it is worth to note that, the molecular weights (Mw) of Chloropyrifos (Mw = 345.5), Malathion (Mw = 230.3), Parathion (Mw = 291.0) and Cypermethrin (Mw = 416.6) is also a participating factor in the extraction step by the foam. These data are also consistent with the general understanding that the larger the molecular weight of the sorbate the larger the amount of the tested insecticides retained on the foam when the substances concerned are similar in nature (El-Shahawi and Aldhaheri, 1995). However, the complex nature of the membrane structure of the polyether foam implies that several mechanisms could be involved simultaneously (Braun *et al.*,1985).

The influence of various concentrations of alkali metal (Li^+, Na^+, K^+, and NH_4^+) chlorides at concentrations $\leq$ 0.1 M on the sorption percentage of the tested compounds at 100 $\mu g/cm^3$ was studied at $4 \leq pH \leq 7$. The results obtained are summarized in Figs. 2.7-2.10. Significant increase in the distribution ratios of Malathion and Parathion (Figs. 2.7 and 2.8) was observed with increasing LiCl or NaCl concentrations from 0.01 to 0.1M and the following order of extraction:

$$Li^+ > Na^+ > NH_4^+ > K^+ \qquad (2.10)$$

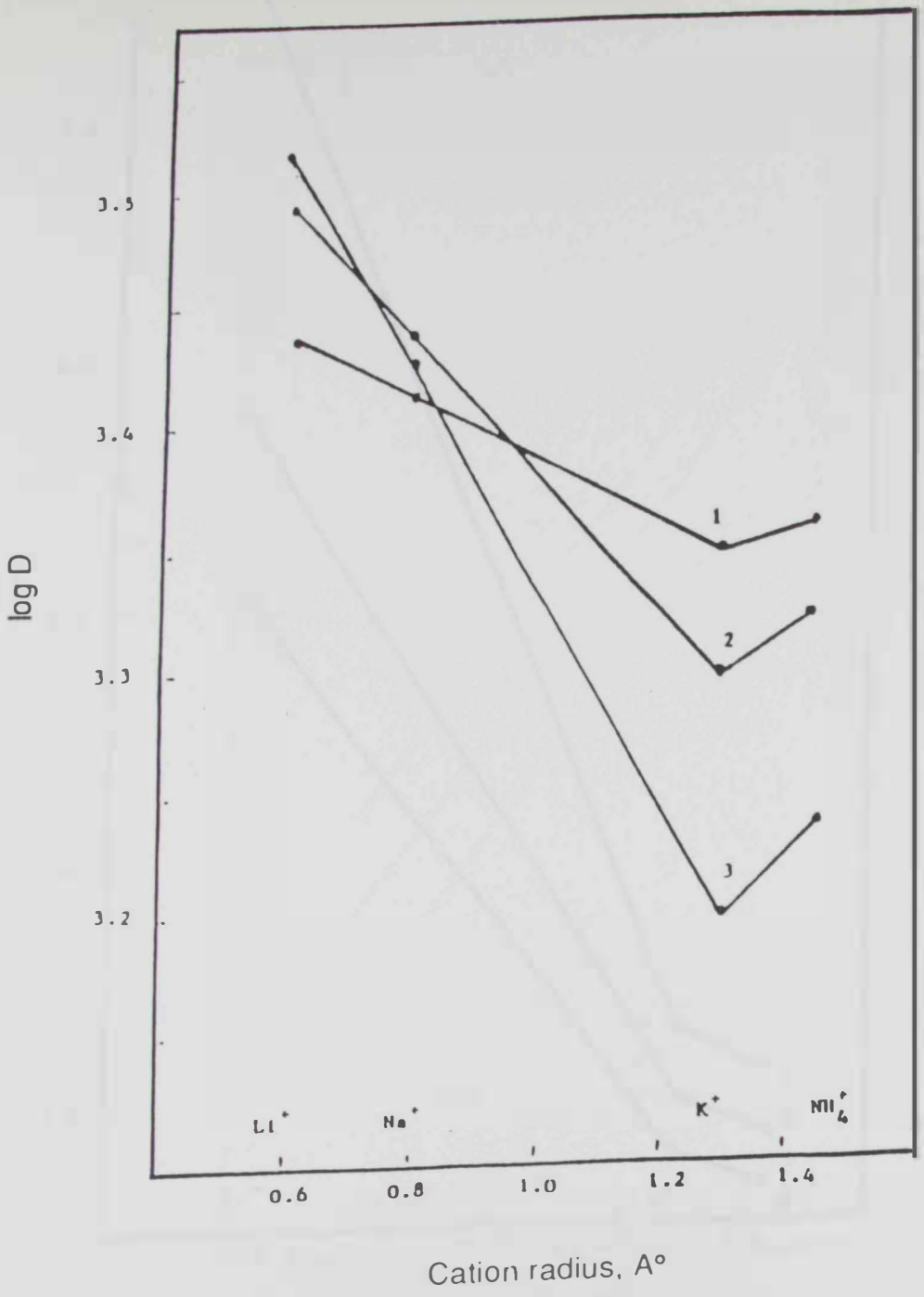


Fig. 2.7. Effect of cation size and concentration (≤ 0.1 M) of various univalent ions (Li^+, Na^+, K^+ and NH_4^+) on the sorption profiles of Malathion by unloaded foams. Salt concentrations are 0.01 M (1), 0.05 M (2) and 0.1 M (3). Other conditions as in Fig. 2.4 and 1hr. shaking time.

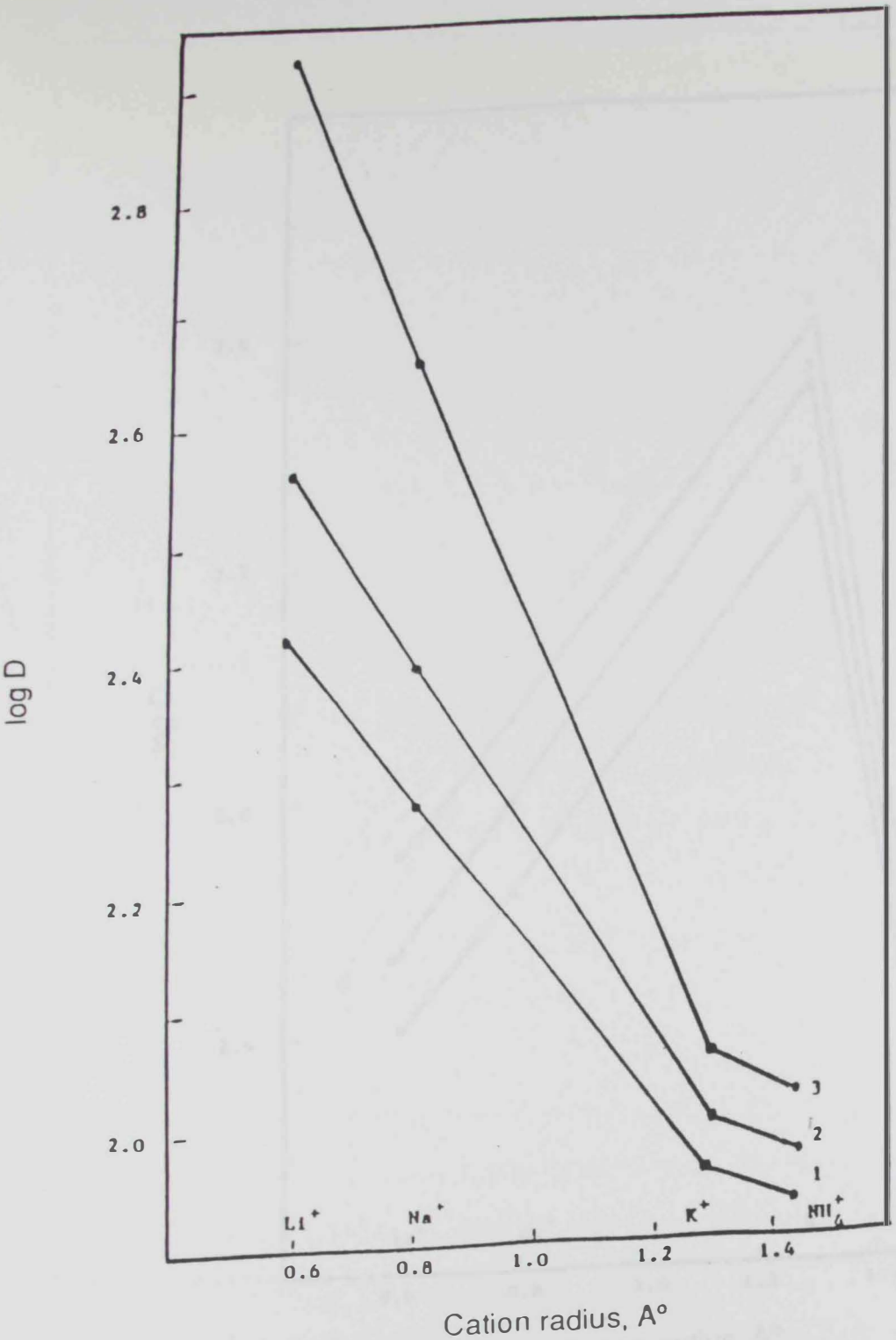


Fig. 2.8. Effect of cation size and concentration (≤ 0.1 M) of various univalent ions (Li^+, Na^+, K^+ and NH_4^+) on the sorption profiles of Parathion by unloaded foams. Salt concentrations are 0.01 M (1), 0.05 M (2) and 0.1 M (3). Other conditions as in Fig. 2.4 and 1hr. shaking time.

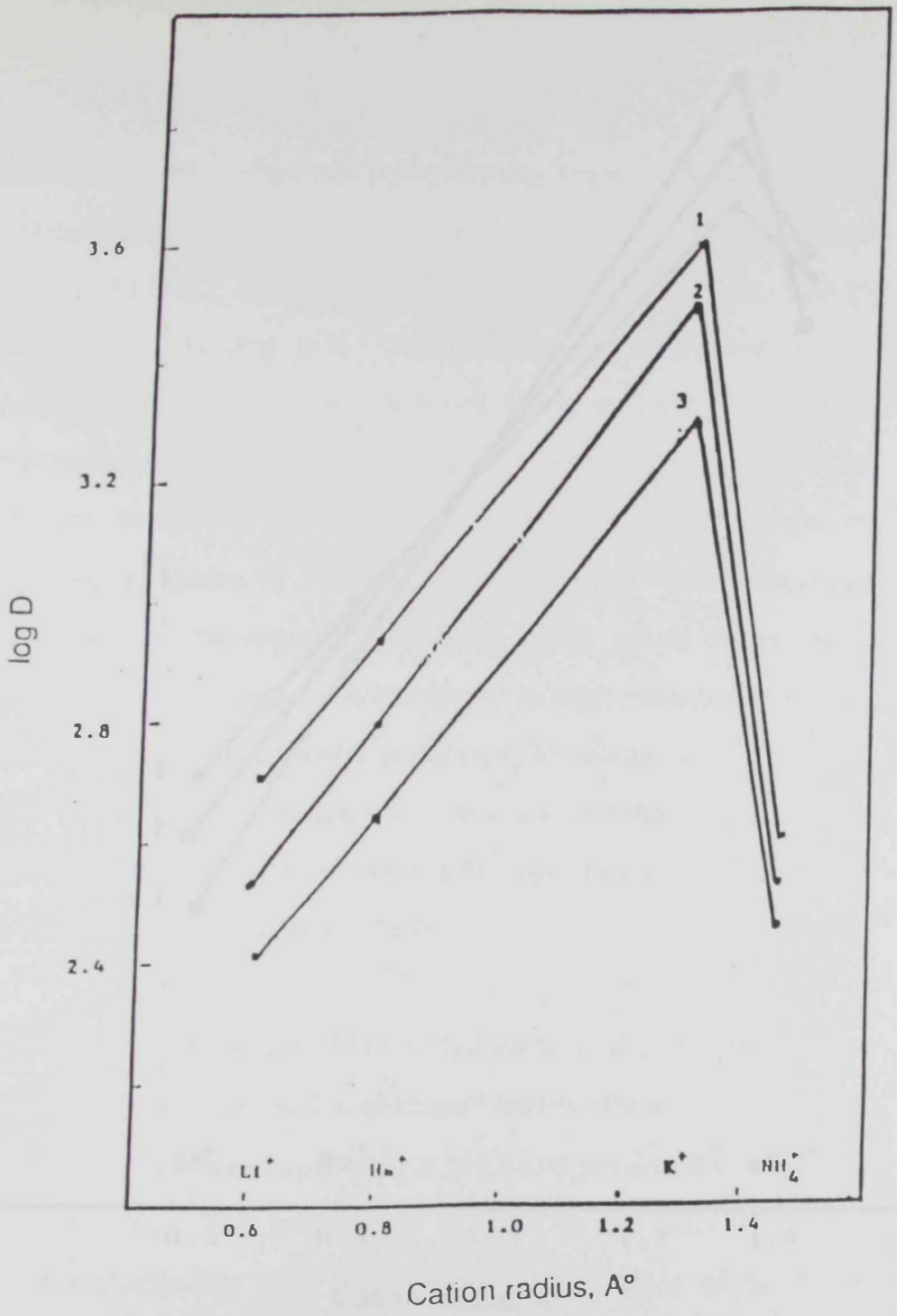


Fig. 2.9. Effect of cation size and concentration (≤ 0.1 M) of various univalent ions (Li^+, Na^+, K^+ and NH_4^+) on the sorption profiles of Cypermethrin by unloaded foams. Salt concentrations are 0.01 M (1), 0.05 M (2) and 0.1 M (3). Other conditions as in Fig. 2.4 and 1hr. shaking time.

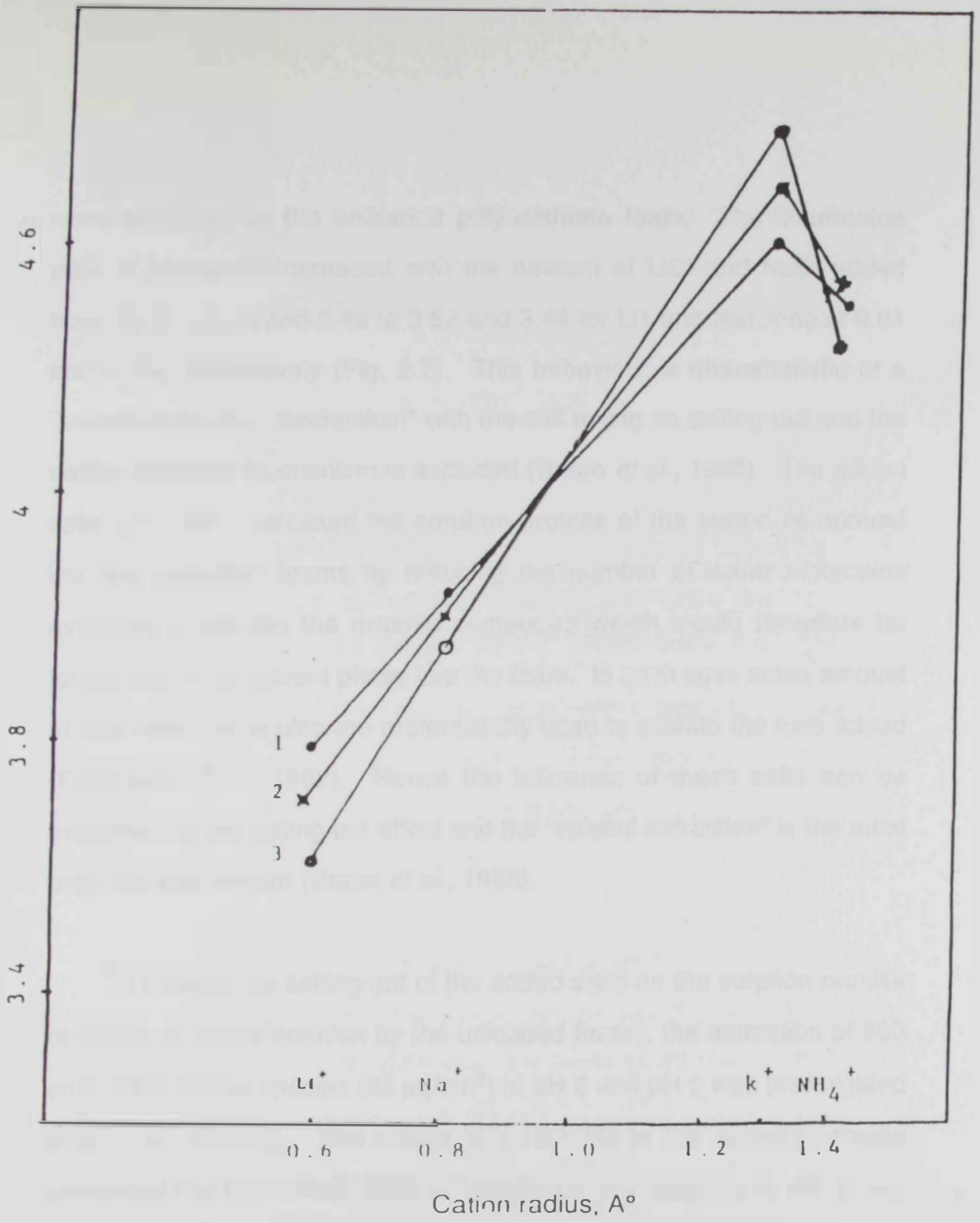


Fig. 2.10. Effect of cation size and concentration (≤ 0.1 M) of various univalent ions (Li^+, Na^+, K^+ and NH_4^+) on the sorption profiles of Chloropyrifos by unloaded foams. Salt concentrations are 0.01 M (1), 0.05 M (2) and 0.1 M (3). Other conditions as in Fig. 2.4 and 1hr. shaking time.

were achieved on the unloaded polyurethane foam. The distribution ratio of Malathion increased with the amount of LiCl and NaCl added from log D = 3.48 and 3.42 to 3.52 and 3.44 for Li^+ and Na^+ ions at 0.01 and 0.1M, respectively (Fig. 2.7). This behaviour is characteristic of a "solvent-extraction mechanism" with the salt acting as salting-out and the cation-chelation mechanism is excluded (Braun *et al.*, 1985). The added salts (Li^+, Na^+) increased the sorption profiles of the tested compound into the polyether foams by reducing the number of water molecules available to solvate the organic compound which would therefore be forced out of the solvent phase into the foam. In such case some amount of free water molecules are preferentially used to solvate the ions added (Fong and Chow 1992). Hence the influence of these salts can be explained by the salting out effect and the "solvent extraction" is the most probable mechanism (Braun *et al.*, 1985).

To confirm the salting out of the added salts on the sorption profiles of Malathion and Parathion by the unloaded foams, the extraction of 200 cm^3 of the former species (80 $\mu g/cm^3$) at pH 2 and pH 6 was investigated after 1 hr. shaking. The added LiCl (0.1 M) to the aqueous media enhanced the distribution ratio of Malathion in a solution of pH 6 (log D=3.05) than at pH 2 (log D=1.9). These results confirm that both Malathion and Parathion tested are highly extractable in the neutral form and the "solvent extraction mechanism" is the more predominant mechanism.

The retention behaviour of Cypermethrin by the unloaded foams (Fig. 2.9) decreased with increasing the concentration of the alkali metal (Li^+, Na^+, K^+, and NH_4^+) chlorides and the following order of sorption:

$$K^+ > Na^+ > NH_4^+ > Li^+ \qquad (2.11)$$

was achieved at 0.1 M salt concentration. Similar behaviour was achieved on the sorption profiles of Chloropyrifos by the foam (Fig. 2.10) in the presence of the same alkali cations. Therefore the ion-dipole interaction of NH_4^+ with the oxygen sites of polyurethane foam might be highly predominant in the sorption of Cypermethrin and Chloropyrifos as compared to Malathion and Parathion. Thus, the cation chelation mechanism may be operative in the sorption process of Cypermethrin and Chloropyrifos (Braun *et al.*, 1985).

According to the "cation-chelation mechanism" the presence of the K^+ ions should facilitate the extraction of the Cypermethrin and Chloropyrifos by the foam more than the other alkali metal ions (NH_4^+, Na^+ or Li^+) because of the better fit of this ion into the central cavity of the oxygen-rich helix in the polyurethane foam. The obtained results of the sorption profiles of Cypermethrin and Chloropyrifos are in good agreement with the data recently reported by Palagyi *et al.*, 1992. Therefore "cation-chelation mechanism" is the most probable mechanism for the sorption of these species. In accordance with this mechanism, the polyalkenoxy chains of the PUF sorbent form a helical

structure. This helical structure of the foam sorbent forms a clathrate with suitable simple cations (Braun *et al.*, 1985).

It has been noted that, temperature remarkably affects the rate of the extractability of the tested insecticides by unloaded polyurethane foam. Thus in batch experiments the influence of temperature (35, 45 and 55 °C) on the sorption profiles of the tested species by the unloaded foam was determined at the pH of maximum extraction of each insecticide. The percentage extractions and the distribution ratios of the tested compounds increased slightly with increasing temperature, and similar trends to that obtained at 20 °C were achieved. Assuming no precipitation or chelation has occurred and the extracted species exist as neutral species in the pH of maximum extractibility, then the equilibrium constant K for the equation.

$$\text{Insecticide}_{aq} \rightleftharpoons \text{Insecticide}_{foam} \qquad (2.12)$$

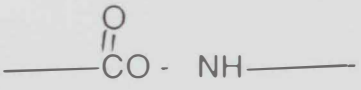
is equivalent to the distribution ratio, D. Thus by plotting ln D vs. $\frac{1}{T}$ and employing the equation:

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}, \qquad (2.13)$$

the values of the standard enthalpy change ΔH° and the standard entropy change ΔS° can be obtained. The ΔS° for Malathion and Parathion were found to be 20±2 and 38±4 J/mol.deg, while for the Cypermethrin and Chloropyrifos the ΔS° values were found to be

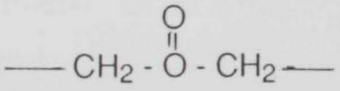
-16 ± 1.8 and -19±2 J/mol. deg., respectively for the sorption into the unloaded foam. The high molecular weight of the Cypermethrin (Mw=416.6) may account for its higher value of $\Delta S°$. The observed decrease in the $\Delta S°$ of Malathion and Parathion is possibly due to the presence of P=S group which could reduce the ion-dipole interaction with the oxygen sites of polyurethane foam. This would reduce the degrees of freedom of movement of the tested organic compounds in the polyurethane foam as previously reported by Adamson, 1967 and Schumack and Chow, 1987 and El-Shahawi, 1994.

The polymeric nature and/or the different functional groups or heteroatoms in the foam may also take a part in the sorption process of both Malathion and Parathion. These data are also consistent with a solvent extraction mechanism and are in good agreement with the data previously reported by Schumack and Chow 1987. The values of the standard enthalpy change, $\Delta H°$ were found to be in the range 26 ± 4 kJ mol^{-1}. Raising the temperature may facilitate the partition of the tested species through the polyurethane foam via urethane linkage (a) and/or ether oxygen atoms (b) as follows:



(a)

or



(b)

The influence of the sorption media on the preconcentration of the tested compounds by the unloaded foams was examined at the optimum pH by the addition of various proportions of ethanol (0-15%). The sorption percentages of Malathion and parathion were decreased by the addition of ethanol up to 15%. Representative results are summarized in Fig. 2.11. This behaviour is probably due to the formation of different association in the aqueous solution (West, 1973). The species present in the aqueous solution are well solvated and so it is difficult for it to form ion-pairs in the aqueous solution. These data are also consistent with the fact that with a compound of low dielectric constant, the degree of extraction should increase with increasing the polarity of the polar phase (Schumack and Chow, 1987). Thus, "solvent extraction mechanism" is the most probable mechanism for the sorption of Malathion and Parathion. In contrary, the sorption profiles of Cypermethrin and Chloropyrifos increased with increasing ethanol concentration. Representative results are summarized in Fig. 2.12. Therefore, the nature of the extraction media has a marked effect on the sorption characteristics of the tested insecticides.

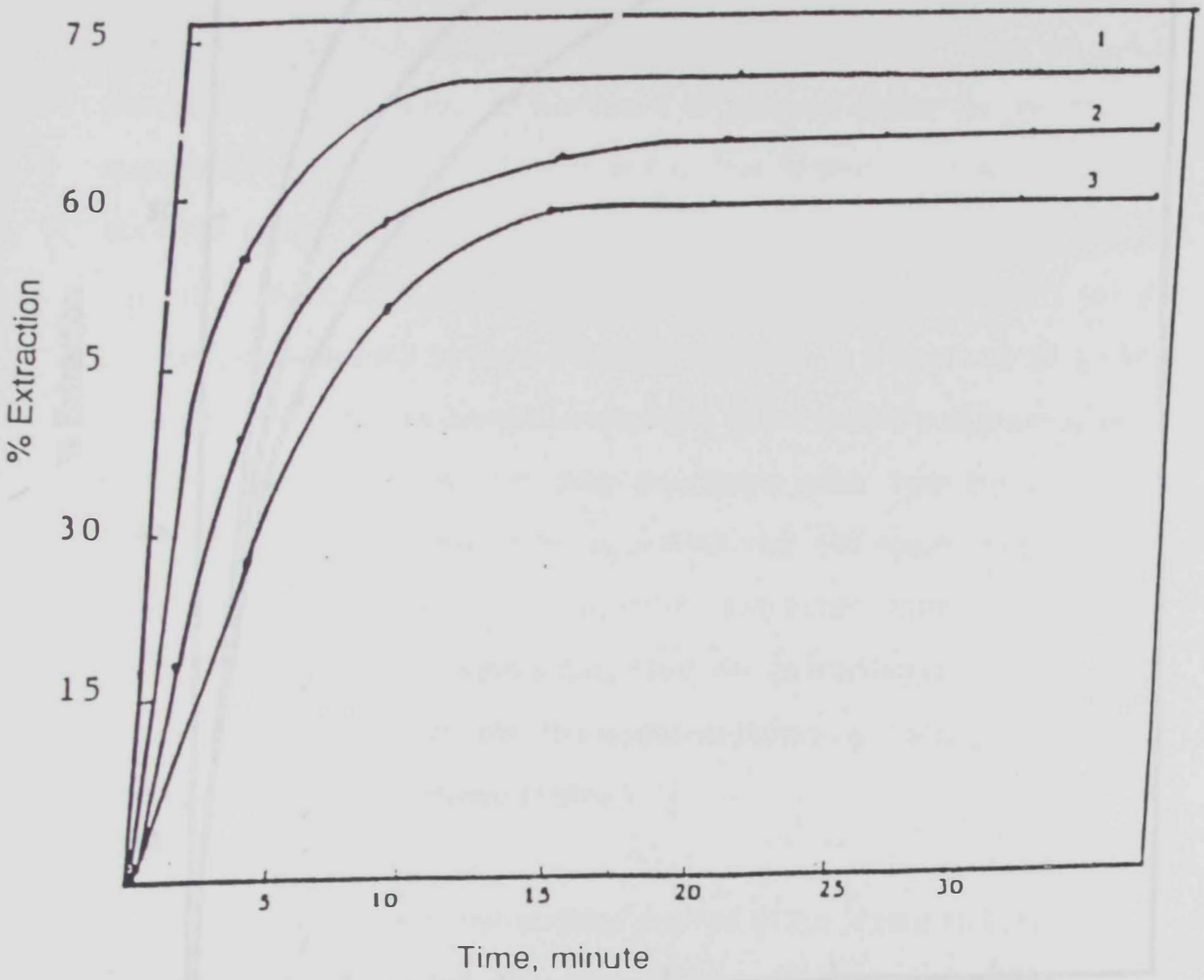


Fig. 2.11. Effect of extraction media on the sorption profile of Malathion by the unloaded foam at 1 hr. shaking time, 0% (1), 5% (2), and 15% (3) of ethanol. Other conditions as in in Fig. 2.4.

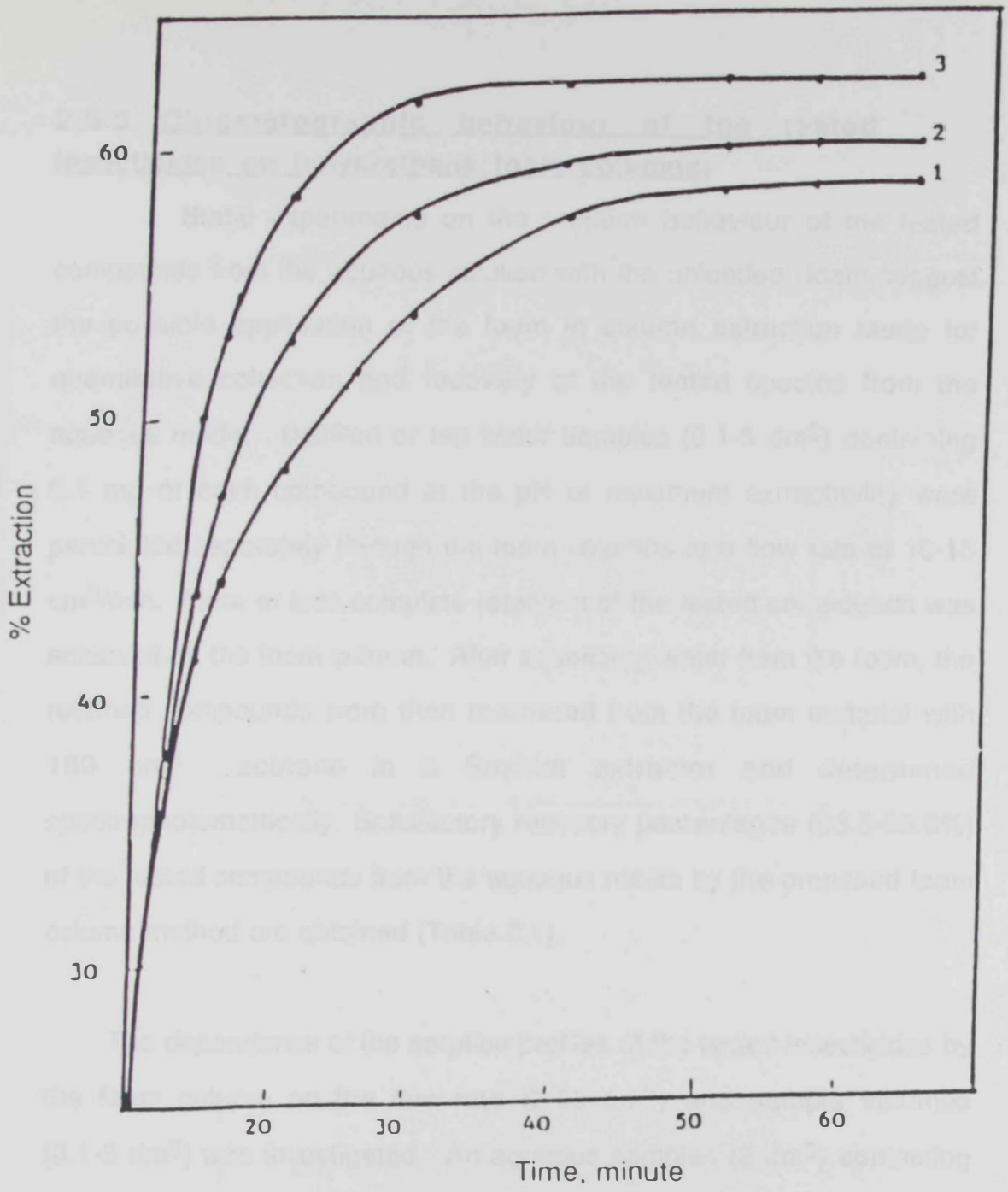


Fig. 2.12. Effect of extraction media on the sorption profile of Cypermethrin by the unloaded foam at 1 hr. shaking time, 0% (1), 5% (2), and 15% (3) of ethanol. Other conditions as in in Fig. 2.4.

2.3.3. Chromatographic behaviour of the tested insecticides on polyurethane foam columns:

Static experiments on the sorption behaviour of the tested compounds from the aqueous solution with the unloaded foam suggest the possible application of the foam in column extraction mode for quantitative collection and recovery of the tested species from the aqueous media. Distilled or tap water samples (0.1-5 dm^3) containing 0.1 mg of each compound at the pH of maximum extractibility were percolated separately through the foam columns at a flow rate of 10-15 cm^3/min. More or less complete retention of the tested compounds was achieved by the foam column. After squeezing water from the foam, the retained compounds were then recovered from the foam material with 100 cm^3 acetone in a Soxhlet extractor and determined spectrophotometrically. Satisfactory recovery percentages (93.5-99.5%) of the tested compounds from the aqueous media by the proposed foam column method are obtained (Table 2.1).

The dependence of the sorption profiles of the tested insecticides by the foam column on the flow-rate (2-25 cm^3) and sample volumes (0.1-6 dm^3) was investigated. An aqueous samples (2 dm^3) containing 0.05 mg of Parathion was percolated through the foam column at various flow-rates up to 25 cm^3/min. Complete retention of Parathion was obtained at flow-rate up to 15 cm^3/min and decreased significantly to 85% at flow-rate 20-25 cm^3/min. On the other hand, on increasing

Table 2.1. Extraction and recovery of the tested compounds from 3 dm^3 distilled and tap water by the proposed unloaded foam column*.

Compound	% Recovery		Wavelength (nm)
	Distilled water	Tap water	
Parathion	95.6 ± 0.4	95.9 ± 0.4	274
Malathion	93.5 ± 0.5	99.5 ± 0.5	206
Cypermethrin	94.2 ± 0.4	95.7 ± 0.7	273
Chloropyrifos	96.5 ± 0.6	97.2 ± 0.4	206

* Average ± SD for five measurements.

sample volume from 2 to 5 dm^3 at flow rate ≤ 15 cm^3/min. no significant decrease on the retention percentage was observed.

To determine the performance of the foam column by the chromatogram method, quantitative retention of Parathion (0.02 mg) followed by elution with 200 cm^3 acetone - HCl (3:1 v/v) through the foam column at 5 cm^3/min flow rate was carried out. The height equivalent to a theoretical plate (HETP) was obtained from the elution curves using the equation (Alfassi and Wai, 1992):

$$N = \frac{8V^2_{max}}{W_e} = \frac{L}{HETP} \qquad (2.14)$$

Where N = number of theoretical plates, V_{max} = volume of eluate at the peak maximum, W_e = width of the peak at $\frac{1}{e}$ the maximum solute concentration and L = length of the column foam bed in mm. The HETP values were found equal 1.9 ± 0.2 and 2 ± 0.2 mm at flow rates of 15 and 20 $cm^3\ min^{-1}$, respectively.

The foam column performance was also calculated from the break through capacity curve method for the tested insecticide (Fig. 2.13). An aqueous solution of Parathion (50 μg/cm^3) was percolated through the column at 10 and 20 cm^3/min and the height equivalent to theoretical plates (HETP) was calculated by employing the equation:

$$N = \frac{V_1.V_2}{(V_1.V_2)^2} = \frac{L}{HETP} \qquad (2.15)$$

where N = number of theoretical plates, V_1 = volume of the effluent at the center of the S-shaped of break through curve where the concentration is one half the initial concentration and V_2 is the volume at which the effluent has a concentration of 0.1578 of the initial concentration. The values of HETP obtained by this method were found in the range 2.1±0.2 mm. The HETP values for Parathion obtained from the chromatogram elution curve at 10 cm^3/min are in agreement with the data obtained from the break through capacity curve method.

The proposed foam column method has been successfully employed for the separation of the binary mixtures of Malathion-Cypermethrin, and Parathion-Cypermethrin insecticides from different volumes (0.1-2 dm^3) of the aqueous media. A mixture contained 0.05 mg of Malathion (or Parathion) was separated from 0.05 mg of Cypermethrin at pH 1.5 and 0.1 M lithium chloride. Sorption of Malathion or Parathion took place while Cypermethrin was not retained on the foam column and collected quantitatively in the effluent. Malathion or Parathion was then recovered from the column by 100 cm^3 acetone in a Soxhlet extractor as described before.

The separation of Malathion (0.1 mg) from Chloropyrifos (0.05 mg) in aqueous solution at pH 2 and in the presence of sodium chloride (0.1 M) has been successfully employed by polyurethane foam. The

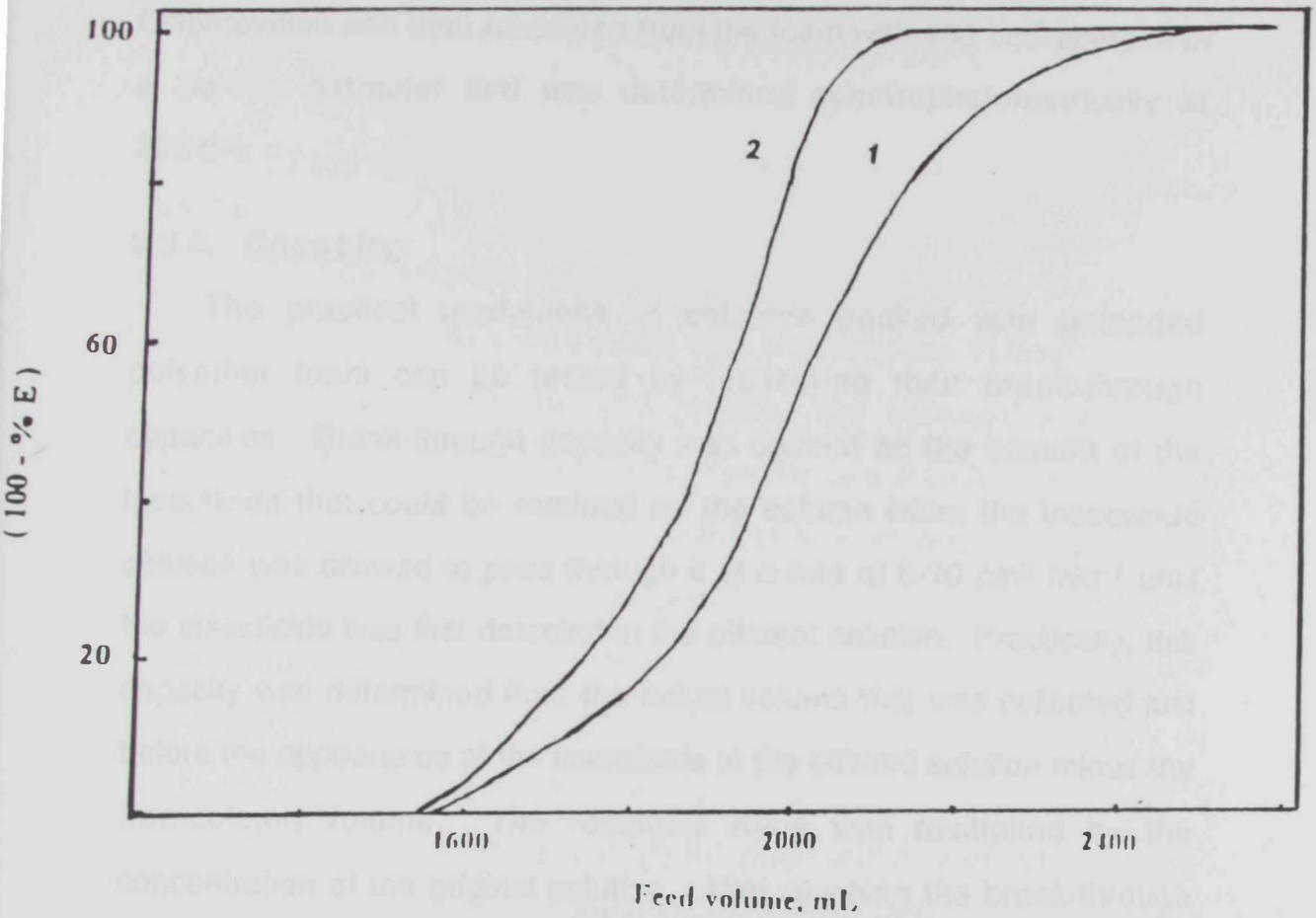


Fig. 2.13. Breakthrough capacity curves of the sorption profiles of Parathion by unloaded foam at flow rates of 10 cm^3 min^{-1} (1) and 20 cm^3 min^{-1} (2) by the unloaded foam column.

solution mixture was percolated through the foam column at 15 cm^3 min^{-1}. Sorption of chloropyrifos took place while Malathion was not retained on the foam column and collected quantitatively in the effluent. Chloropyrifos was then recovered from the foam with 100 cm^3 acetone in a Soxhlet extractor and was determined spectrophotometrically at 206 nm.

2.3.4. Capacity:

The practical usefulness of columns packed with unloaded polyether foam can be tested by measuring their break-through capacities. Break-through capacity was defined as the amount of the insecticide that could be retained on the column when the insecticide solution was allowed to pass through it at a rate of 5-10 cm^3 min^{-1} until the insecticide was first detected in the effluent solution. Practically, this capacity was determined from the actual volume that was collected just before the appearance of the insecticide in the effluent solution minus the free-column volume. The resultant value was multiplied by the concentration of the original solution. After reaching the break-through volume, elution was continued until the effluent solution concentration reached that of the feed solution. The curves of Fig. 2.13 present the break-through volume and the volume needed to reach bed saturation for Parathion (50 μg cm^{-3}) at the optimum pH at 5-10 and 15-20 cm^3/min flow rate. It is clear from the curves that the rising portions have large slopes which indicates both a high transfer rate of Parathion in the membranes forming the skeleton of the foam material and that the

absorption equilibrium of the tested compound on the unloaded foam material can be attained rapidly. The break through and overall capacities of foam column packed with one gram dry foam for Parathion are 0.4 and 0.35 mg respectively at 5-10 and 15 cm^3 min^{-1}.

2.3.5. Effect of Chloropyrifos Treatment on Tomato and Parsley Plants:

Total trace element analysis of Tomato and Parsley plants was performed before(1) and after spray with Chloropyrifos in water (0.04% w/v) for 24 (2), 72 (3) and 120 (4) hrs. The obtained results are summarized in Table 2.2 and 2.3 for Tomato and Parsley respectively. The overall average concentration pattern of N, K, P, Na, Fe, Zn, Mn and Copper (Table 2.2) follow the sequence:

$$2 > 1 > 3 > 4$$

$$2 > 1 > 3 > 4$$

$$1 > 3 > 2 > 4$$

for iron (55-110 ppm), manganese (40-61 ppm) and copper (16-41 ppm), respectively. The observed decrease in these essential elements is possibly attributed to the great ability of Chloropyrifos to penetrate through plant tissues and complexing with these metal ions. Accumulation of these complexes decrease the uptake of these metal ions (Corbett, 1974). No significant change in the uptake of Zinc (12 ppm). For nitrogen (3.2-3.4%), potassium (0.75-0.87%), phosphorous (0.43-0.46%) and sodium (0.29-0.36%). The accumulation pattern of these elements follow, respectively the sequence:

1 > 4 > 3 > 2

3 > 2 > 1 > 4

4 > 3 > 2 > 1

2 > 4 > 1 > 3

In plant Parsley, the distribution of phosphorous (0.39-0.50%) and copper (7-8 ppm) before and after spray (Table 2.3) follow the sequence:

4 > 3 > 2 > 1

while for nitrogen (3.1-3.8%) and potassium (1.9-2.6%) the uptake follow the order:

3 > 4 > 2 > 1

In the case of sodium (0.9-1.5%) and iron (60-72.5 ppm) the distribution follow the sequence:

1 > 2 > 4 > 3

while for zinc (30.5-34 ppm) and manganese (31-35 ppm) the uptake follow the sequence:

4 > 3 > 2 > 1

3 > 4 > 2 > 1

respectively. These results show increase in the uptake of phosphorous and copper with increasing spray time by Chloropyrifos and decrease in the uptake of sodium and iron. These results may attributed to the influence of Chloropyrifos in the plant tissues.

Tables 2.3 and 2.4 show the effect of Chloropyrifos on the percentages of humidity, wet weight and dry weight for Tomato and Parsley plants. In plant Tomato (Table 2.3) the percentages of humidity (78.4-86.1%), dry weight (2.1-7.5%) and wet weight (11.8-17.8%) the distribution pattern, respectively follow the sequence:

$$2 > 1 > 3 > 4$$

$$3 > 4 > 1 > 2$$

$$3 > 4 > 2 > 1$$

In plant Parsley (Table 2.4), more or less similar observation on the humidity, (78.4-81%), dry weight (2.3-3.8%) and wet weight (12.3-17.6%). The distribution pattern, respectively follow the sequence:

$$2 > 3 > 1 > 4$$

$$4 > 2 > 1 > 3$$

$$4 > 2 > 3 > 1$$

These results suggest similar mode of action of Chloropyrifos on the humidity percentages of plant Tomato and Parsley. More or less similar mode of action of Chloropyrifos on the dry and wet weight was also achieved of both Tomato and Parsley tissues untreated and treated with Chloropyrifos for different intervals 0-120 hrs.

Table 2.2. Total trace element of plant Tomato before and after spraying with Chloropyrifos in water (0.04% w/v).

S.No.	Type	Percentage, %				Concentration, ppm			
		N	K	P	Na	Fe	Zn	Mn	Cu
1	Tomoto before spray	3.36 3.53	0.80 0.80	0.44 0.43	0.28 0.34	80.0 120.0	12.0 12.0	55.0 56.0	42.0 40.0
	Average	3.45	0.80	0.43	0.31	100.0	12.0	55.5	41.0
2	Tomato after spray 24 hrs.	3.19 3.12	0.82 0.90	0.45 0.48	0.33 0.38	100.0 120.0	11.0 12.0	70.0 52.0	26.0 26.0
	Average	3.16	0.86	0.46	0.36	110.0	11.50	61.0	26.0
3	Tomato after spray 72 hrs.	3.25 3.19	0.86 0.88	0.44 0.46	0.29 0.29	80.0 80.0	12.0 12.0	45.0 45.0	30.0 30.0
	Average	3.22	0.87	0.45	0.29	80.0	12.0	45.0	30.0
4	Tomato after spray 120 hrs.	3.36 3.36	0.75 0.75	0.46 0.46	0.33 0.30	50.0 60.0	11.0 13.0	40.0 40.0	16.0 16.0
	Average	3.36	0.75	0.46	0.32	55.0	12.0	40.0	16.0

Table 2.3. Total trace element of plant Parsley before and after spraying with Chloropyrifos in water (0.04% w/v).

S.No.	Type	Percentage, %				Concentration, ppm			
		N	K	P	Na	Fe	Zn	Mn	Cu
1	Parsley before spray	3.08 3.08	1.80 2.00	0.39 0.40	1.50 1.50	70.0 75.0	30.0 31.0	30.0 32.0	8.0 6.0
	Average	3.08	1.90	0.39	1.50	72.5	30.5	31.0	7.0
2	Parsley after spray 24 hrs.	3.64 3.70	1.90 2.04	0.40 0.45	1.47 1.48	60.0 80.0	30.0 35.0	35.0 32.0	8.0 6.0
	Average	3.67	1.97	0.43	1.48	70.0	32.5	33.5	7.0
3	Parsley after spray 72 hrs.	3.81 3.81	2.60 2.60	0.41 0.45	0.90 0.95	60.0 60.0	33.0 35.0	35.0 35.0	8.0 8.0
	Average	3.81	2.6	0.43	0.92	60.0	34.0	35.0	8.0
4	Parsley after spray 120 hrs.	3.75 3.75	2.52 2.52	0.50 0.50	1.05 1.05	70.0 60.0	33.0 35.0	35.0 35.0	8.0 8.0
	Average	3.75	2.52	0.50	1.05	65.0	34.0	35.0	8.0

Table 2.4. Humidity, % and weight (g) calculation of plant Tomato before and after spraying with Chloropyrifos in water (0.04%).

S.No.	Sample Name	Wet Wt.	Dry Wt.	Humidity, %
1	Tomato before spray	12.08 11.47	2.26 1.99	81.2 82.6
	Average	11.78	2.13	81.9
2.	Tomato after 24 hrs. spray	16.35 13.27	2.40 1.75	85.3 86.8
	Average	14.81	2.08	86.1
3.	Tomato after 72 hrs. spray	21.73 13.83	6.66 8.39	79.8 82.2
	Average	17.78	7.53	81.0
4	Toamto after 120 hrs. spray	19.45 15.68	4.39 2.46	78.5 78.3
	Average	17.57	3.43	78.4

Table 2.5. Humidity, % and weight (g) calculations of plant Parsley before and after spraying with Chloropyrifos in water (0.04%).

S.No.	Sample Name	Wet Wt.	Dry Wt.	Humidity, %
1	Parsley before spray	9.96 14.62	2.22 2.87	77.7 80.4
	Average	12.29	2.55	79.0
2.	Parsley after 24 hrs. spray	18.66 12.55	3.57 2.36	80.9 81.2
	Average	15.61	2.97	81.0
3.	Parsley after 72 hrs. spray	15.62 14.02	1.87 2.86	80.4 79.6
	Average	14.32	2.34	79.9
4	Parsley after 120 hrs. spray	19.45 15.68	4.19 3.41	78.5 78.25
	Average	17.57	3.80	78.4

CHAPTER 3

SENSITIVE DETECTION AND SEMIQUANTITATIVE DETERMINATION OF BISMUTH(III) WITH SOME CHROMOGENIC REAGENTS IMMOBILIZED ON POLYURETHANE FOAMS

3.1. INTRODUCTION

Bismuth is present in sea water, marine animals, and land plants in very low amounts. Even smaller amounts are found in land animals, probably as a result of the limited gastrointestinal absorption. Two forms of toxicity due to bismuth have been described in man: parenteral administration of various bismuth containing compounds has resulted in an "epithelial-cutaneous" form of toxicity, whereas oral ingestion on bismuth subgallate and bismuth subnitrate has led to a "neurotoxicity" in some patients with the development of a reversible metabolic encephalopathy (Emmerling *et al.*, 1986).

In view of the significant production and widespread use of bismuth and its compounds, some must enter the environment and food chains. Bismuth is not detectable in rain water, soil solutions or river waters. However, it is detectable in sea water but in low concentration. Small amounts of bismuth are excreted in the urine, indicating some gastrointestinal absorption, with small amounts also being detectable in blood (Bruland, 1983). The amounts of bismuth observed in various life forms are considered to be without harmful effect. However, in man quite considerable accumulations of bismuth can develop under specific circumstances, and these have resulted in two distinct forms of toxicity (Bruland, 1983).

Several methods have been reported for the analysis of bismuth such as multi-element preconcentration of soil and sediment, anodic stripping voltammetry, rapid chelatometric determination, atomic absorption spectrometry with hydride generation and electrothermal atomic absorption spectrometry after liquid-liquid extraction. Spectrophotometric methods involving formation of bismuth(III) with mucic acid, dithizone, xylenol orange and tetra-n-butylammonium tetraiodobismuthate(III) have been also reported (El-Shahawi and Kamal, 1995). However, most of these methods are expensive, required preconcentration of bismuth and are very laborious and not practicable in routine analysis of bismuth (El-Shahawi and Aldhaheri, 1995).

Spot test analysis is presently the method of highest potential value for the rapid and sensitive identification of the great majority of anions and cations (Feigl and Anger, 1972) and also many organic materials (Feigl, 1956). The most useful kind of spot test, consists in bringing a drop of the test solution together with a drop of the appropriate reagent solution on a suitable substrate such as micro test tube, spot plate or filter paper.

Two important developments are made to the qualitative analysis of inorganic substances: the ring-oven technique and the resin-spot tests (Weisz, 1970). In the ring-oven method, the substances to be detected or determined are concentrated in the form of sharp, well defined zones.

This is carried out by placing a drop of the test solution (as low as 1 mm^3) on around filter paper which is placed on the ring-oven and the components are washed into the ring zone with a suitable solvent.

Resin-spot tests can be considered as special kind of spot reaction in which traces of ions to be detected are concentrated first on the external surfaces of few ion-exchange bands (Weisz, 1970). The adsorbed ions are then allowed to react with the appropriate reagents, under suitable experimental conditions, to produce coloured products which can be observed in the small space of the resin surface.

The application of polyurethane foam loaded with water-insoluble reagents, which yield coloured reaction products, were found to be very attractive for raising the sensitivity of spot tests (Braun and Farag, 1975a). These tests were proved to be more sensitive than normal spot test on spot plate, paper impregnated with the suitable reagent and resin-spot test (Farag *et al.*, 1981). Good selectivities were illustrated by the detection of Cobalt(II) ions in the presence of relatively high excess of diverse elements (Braun and Farag, 1975b).

Polyurethane foam loaded with biacetylmonooxime benzoyl-hydrazone, dithizone and lead diethyldithiocarbamate, have been used for qualitative and semiquantitative determination of cobalt(II), chromium(VI), iron(III), and nickel(II) in aqueous solution using

polyurethane foams loaded with Amberlite LA-1, 1,5-diphenyl carbazide, tricaprylyl amine and dimethylglyoxime, respectively. Furthermore, semiquantitative determination of these metal ions were successfully carried out in both static and dynamic experiments (Braun *et al.*, 1985).

The application of plasticized and unplasticized 1-(2-pyridylazo-2-naphthol) (PAN) polyurethane foams was studied in batch and column test for low detection limit of metal ions and the results showed better performance for the plasticized reagent foam than the unplasticized one. The sensitivity of the chromofoam was shown to be much better than normal spot test on spot plate, paper impregnated with reagent and resin spot test (Fiegl and Anger, 1972). Semiquantitative analysis is carried out either by comparing the coloured of the end product with colour scales in batch operation by measuring coloured zones on the packed column after percolating the test solution (Braun and Farag, 1974c). In the batch method the density of the colour on the foam cube was found to be dependent on the concentration of the metal in the solution.

Farag *et al*, 1986, 1987, 1989 and 1992 have applied many reagent-loaded polyurethane foam for the detection and semiquantitative determination of lead(II) in urine, copper(II) in raw and contaminated river water, palladium(II), cadmium(II), silver(I), bismuth(III), zinc(II), cobalt(II) and mercury(II). Results were successful and demonstrated

that the detection limit of these metals were much better compared with usual spot test method (Feigl and Anger, 1972).

This chapter work was carried out in an attempt to use the loaded and unloaded polyurethane foam with dithizone and 1,5-di(2-fluorophenyl)-3-mercaptoformazan for the detection and semiquantitative determination of bismuth(III) in water using batch, dynamic and pulsating column techniques. The effect of foreign ions on the detection limits of bismuth(III) was also investigated. The proposed methods are based on the formation of coloured chelates with bismuth(III) and subsequent preconcentration of the produced chelates on the polyether based polyurethane foam.

3.2. EXPERIMENTAL

3.2.1. Apparatus:

A Shimadzu UV-2101 PC UV-visible scanning spectrophotometer with 10 mm quartz cells and a Shimadzu FTIR-8101 Fourier Transform Infrared Spectrophotometer were used for recording the electronic and vibrational spectra of the reagents and their bismuth(III) complexes. Philips digital pH-meter (Model 9418) with glass and Saturated Calomel Electrodes was used for the pH measurement. Glass columns (5 mm diameter and 160 mm height) and pulsating column (medical syringes, 100 cm^3 capacity) were also used in dynamic and pulsating flow techniques.

3.2.2. Reagents and Materials:

All reagents used were of analytical reagent grade, except otherwise mentioned.BDH dithizone (H_2Dz) and tri-n-butylphosphate (TBP) were used without further purification. Polyurethane foam, a polyether of open-cell type was supplied by Greiner, K.G. Schaumstoffwerk-Kremsmunster, Austria. The bulk density of the foam material was 30 kg m^{-3}. The foam (cubes of 5 mm edge) was washed with 1M hydrochloric acid followed by distiled water until the washings (water) were free from chloride ion. The foam material was then washed with acetone and dried at 80 °C. Stock solution containing 1 mg cm^{-3} of bismuth(III) was prepared by dissolving $Bi(NO_3)_3.9H_2O$ (BDH) in

dionized water acidified with few drops of 0.5M nitric acid and standardized by EDTA titrations. A series of standard bismuth(III) solutions was prepared by diluting the stock solution with water acidified with few drops of 0.5M nitric acid. For the purpose of studying the influence of various cations and anions on the detection of 1 µg of bismuth(III) stock solutions of various metal ions were prepared from their nitrates, chlorides, sulphates and bromides, so as to contain 10 mg. cm^{-3}. Stock solution of anions were prepared from their alkali or ammonium salts.

3.2.3. Synthesis of the Reagent 1,5-di(2-fluorophenyl)-3-mercaptoformazan:

1,5-di(2-fluorophenyl)-mercaptoformazan (F_2H_2Dz) prepared by the nitroformazyl method (Kiwan and Kassim, 1977). The nitroformazan was recrystalized from ethanol and converted to 1,5-di(2-fluorophenyl)-mercaptoformazan by the normal procedure and was finally purified by dissolution in chloroform, extraction with dilute (2% w/v) sodium hydroxide solution and finally pouring the extract into 0.5M sulphuric acid. The solid reagent was washed with ethanol, dried, dissolved in chloroform, precipitate with cyclohexane and then dried in vacuo. The reagent and its bismuth(III) complexes were characterized on the basis of their electronic spectra, characteristic IR frequencies and elemental analysis.

3.2.4. Reagent Foam Preparation:

The dithizone (Merck) and the reagent 1,5-di(2-fluorophenyl)-3-mercaptoformazan solutions were prepared by dissolving 10 mg of each reagent in 50 ml chloroform. The F_2H_2Dz and H_2Dz-foam was prepared by mixing the dried foam cubes with F_2H_2Dz- and H_2Dz solutions (10 ml g^{-1} dry foam), respectively with efficient stirring for 10 min. The reagent-loaded foam was then squeezed and dried as reported (Braun and Farag, 1975). The plasticized F_2H_2Dz- and H_2Dz-foam was prepared by mixing the dried foam cubes with the reagent in TBP (0.1% w/v), respectively with efficient stirring for 15 min and dried as reported (Braun and Farag, 1975c).

3.2.5. Column Preparation for Dynamic Experiments:

Column preparation is of capital importance in all types of chromatographic techniques. Vacuum method for foam column packing has been developed by Braun, *et al.*, 1985 and was employed in the present work. In this method, about 0.2 g loaded or unloaded foam with the chromogenic reagents, H_2Dz or F_2H_2Dz were packed in the column applying gentle pressure with a glass rod (Fig. 3.1). To avoid air bubbles during packing, tap (1) was connected to a suction pump, while tap (2) was closed after about 5 min of evacuation, distilled water was allowed to fill the column gradually through the funnel (2).

3.2.6. General Procedures:

3.2.6.1. Batch experiments: One reagent-loaded or plasticized reagent TBP foam cube is shaken with 3-5 ml of the bismuth(III) in

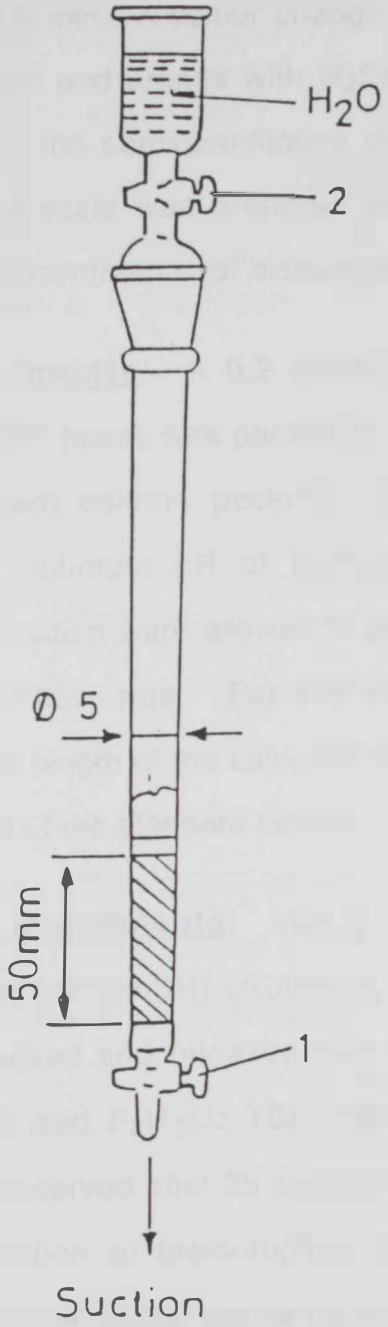


Fig. 3.1. Foam column in packing step.

aqueous solution (pH < 5.2) for 5 min. A colour change of the reagent foam from green to orange-brown and orange with H_2Dz and F_2H_2Dz, respectively was observed. For the semiquantitative determination of bismuth(III), a standard colour scale was prepared with a series of standard solutions of different concentrations of bismuth(III).

3.2.6.2. Column flow experiments: A 0.2 gram of the reagent loaded or plasticized reagent TBP foams was packed in a glass column by the vacuum method of foam column packing. 250 ml of the bismuth(III) solution at the optimum pH of bismuth(III)-HDz or bismuth(III)-F_2HDz complex formation were allowed to pass through the foam column at 2-3 ml min^{-1} flow rate. For the semiquantitative determination of bismuth(III) the length of the coloured zone of the foam bed is then compared with those of the standard series.

3.2.6.3. Pulsating column experiments: Into a 100 ml medical syringe transfer 50 ml of the test bismuth(III) solution at the suitable pH. The solution was then compressed and released with one cube foam loaded with F_2H_2Dz or plasticized F_2H_2Dz-TBP-foam. The colour change of the foam cube was observed after 25 successive pulses. For the semiquantitative determination of bismuth(III), the solution was compared with a standard colour scale prepared from a series of standard bismuth(III) solution and the reagent F_2H_2Dz or H_2Dz loaded foam cube at the same number of pulses.

3.3. RESULTS AND DISCUSSION

The most common reported spectrophotometric procedures for bismuth(III) determination involve chelation with mucic acid, xylenol orange, Cyanex 301, and formation of the ion-associate tetramethylammoniumbismuthate (El-Shahawi and Aldhaheri, 1995; and Argekar and Shetty, 1995). However, most of these methods are expensive, not practical in routine analysis, suffer from lack of selectivity detection limit and require a laborious enrichment step e.g. precipitation, floatation etc.

In recent years considerable interest is focused currently on the chromofoam test due to its sensitivity and simplicity. Open cell polyurethane foam (PuF) have been successfully used in the retention and collection of various species and organic solvents by swelling (El-Shahawi *et al.*, 1994 and 1995). Foams loaded with dithizone and other organic reagents (chromofoams) have been reported for the sensitive detection and semiquantitative determination of some metal ions including bismuth(III) employing batch and column extraction modes (Hamza *et al.*, 1990).

This technique simply allow the loading of the foam material with various organic reagents dissolved in hydrophobic organic solvents. Tri-n-butylphosphate (TBP) which is employed in the present work as a stationary phase acts as a plasticizer to the foam material (Braun *et al.*,

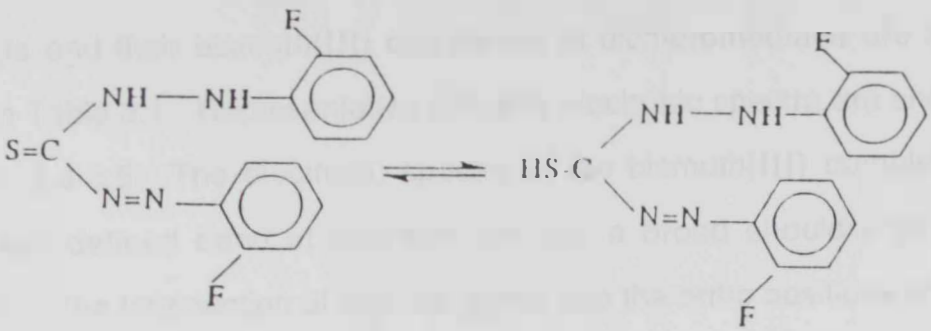
1985). It is well known that the diffusion of ions through the so called "solvent membrane" is generally enhanced by the presence of plasticizer (El-Shahawi, 1994). Also the application of plasticizer in preparing reagent foams was found to improve the extraction of metal ions on the reagent foams (Farag and El-Nemma, 1992).

Bismuth(III) forms an orange-red and orange-brown coloured complexes with 1,5-di-(2-fluorophenyl)-3-mercaptoformazan, I and dithizone II in acidic aqueous solution (pH < 5.2), respectively. The structure of the tested chelating agent is given in Fig. 3.2. The predominant equilibrium in dilute aqueous solution between bismuth(III) and the tested chelating agents proceeds as follows:

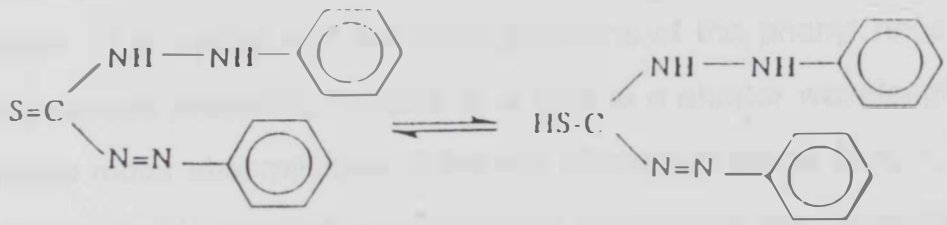
$$Bi^{3+} + F_2H_2Dz \quad ====== \quad Bi(F_2HDz)_3 + 3H^+ \qquad (3.1)$$

$$Bi^{3+} + H_2Dz \quad ====== \quad Bi(HDz)_3 + 3H^+ \qquad (3.2)$$

The complexes formed are readily extracted by non-polar organic solvents without change in colour (El-Shahawi and Al-Mehrezi, 1995).



1,5-di-(2-fluorophenyl)-3-mercaptoformazan (F_2H_2Dz)



1,5-di-(phenyl)-3-mercaptoformazan (H_2Dz)

Fig. 3.2. Structure of the tested chelating agents.

Table 3.1 summarizes the I.R. data for the regions of interest in the I.R. spectra of the solid reagents H_2Dz and F_2H_2Dz and their solid complexes with bismuth(III). The electronic absorption spectra of the reagents and their bismuth(III) complexes in dichloromethane are also given in Table 3.1. Representative I.R. and electronic spectra are shown in Figs. 3.3-3.5. The electronic spectra of the bismuth(III) complexes have well defined band at 490-498 nm and a broad shoulder of low intensity. The introduction of fluorine atoms into the ortho positions of the phenyl nuclei of dithizone leads to small bathochromic shifts in both its bands, viz., 632 and 454 nm vs 620 and 450 nm, respectively for dithizone. The position of the λ_{max} for the bismuth complex of F_2H_2Dz underwent similar shifts (Table 3.1) as compared to bismuth(III) complex of H_2Dz. The shifts do not follow the general statement that "the introduction of a radical into the ortho positions of the phenyl rings of dithizone causes practically no shift or a shift to a shorter wavelength". The relative molar absorptivities of the two absorption bands of F_2H_2Dz and its bismuth(III) complex were similarly affected by the introduction of fluorine atoms compared to H_2Dz and its bismuth(III) complex (Table 3.1). The reagents H_2Dz and F_2H_2Dz form 1:3 complexes with bismuth(III) as previously reported (Kiwan and Kassim, 1977).

In the I.R. spectra of the reagents H_2Dz and F_2H_2Dz a broad absorption band at 3360-3460 (br.) cm^{-1} was observed and assigned to the stretching frequency of a strongly hydrogen bonded NH group. This

Table 3.1. Characteristic absorption I.R. (cm^{-1}) and electronic (nm) spectral data for the reagents F_2H_2Dz and H_2Dz and their bismuth(III) chelates in KBr discs*.

Compound	υ (N-H)	δ(N-NH)+(C=N)	υ(N-C-S)	λ_{max} (nm)	∈ ($x10^3$ mol^{-1} cm^{-1})
F_2H_2Dz	3360 (br)	1510 (s)	1485 (s) 1450 (s)	632 454	25.3 23.7
H_2Dz	2460 (br)	1515 (s)	1505 (s) 1465 (s)	615 654	35.8 17.9
$Bi(F_2HDz)_3$	3440 (m) 3245 (m) 3090 (br)	1535 (s)	1485 (s) 1460 (s) 1440 (m)	497	91.4
$Bi(HDz)_3$	3420 (m) 3190 (m) 3060 (m)	1530 (s)	1490 (s) 1480 (sh)	495	80

* s = strong ; m = medium ; w = weak ; sh = shoulder and br = broad.

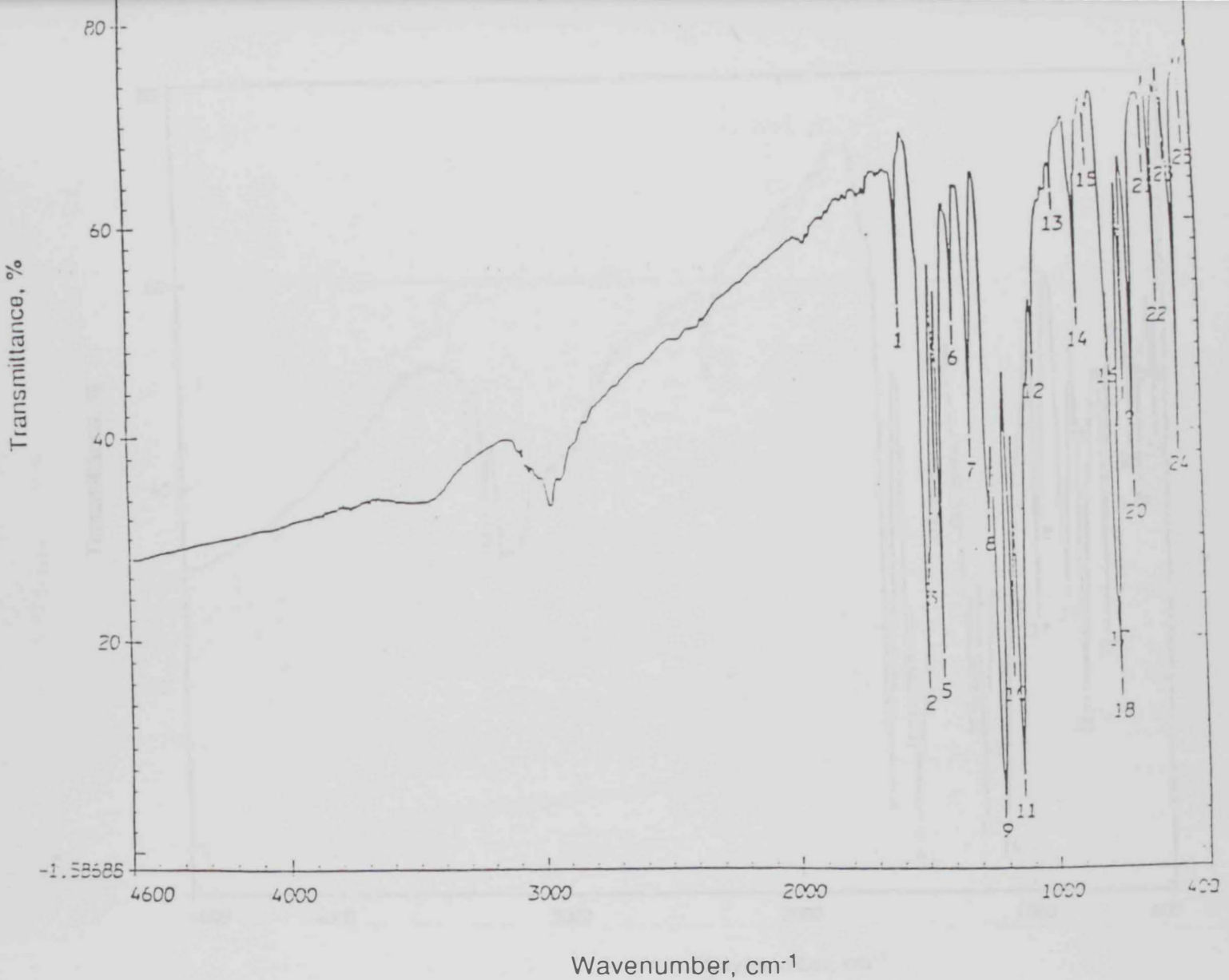


Fig. 3.3. Infrared spectrum of 1,5-di-(2-fluorophenyl)-3-mercaptoformazan (F_2H_2Dz) in potassium bromide desk.

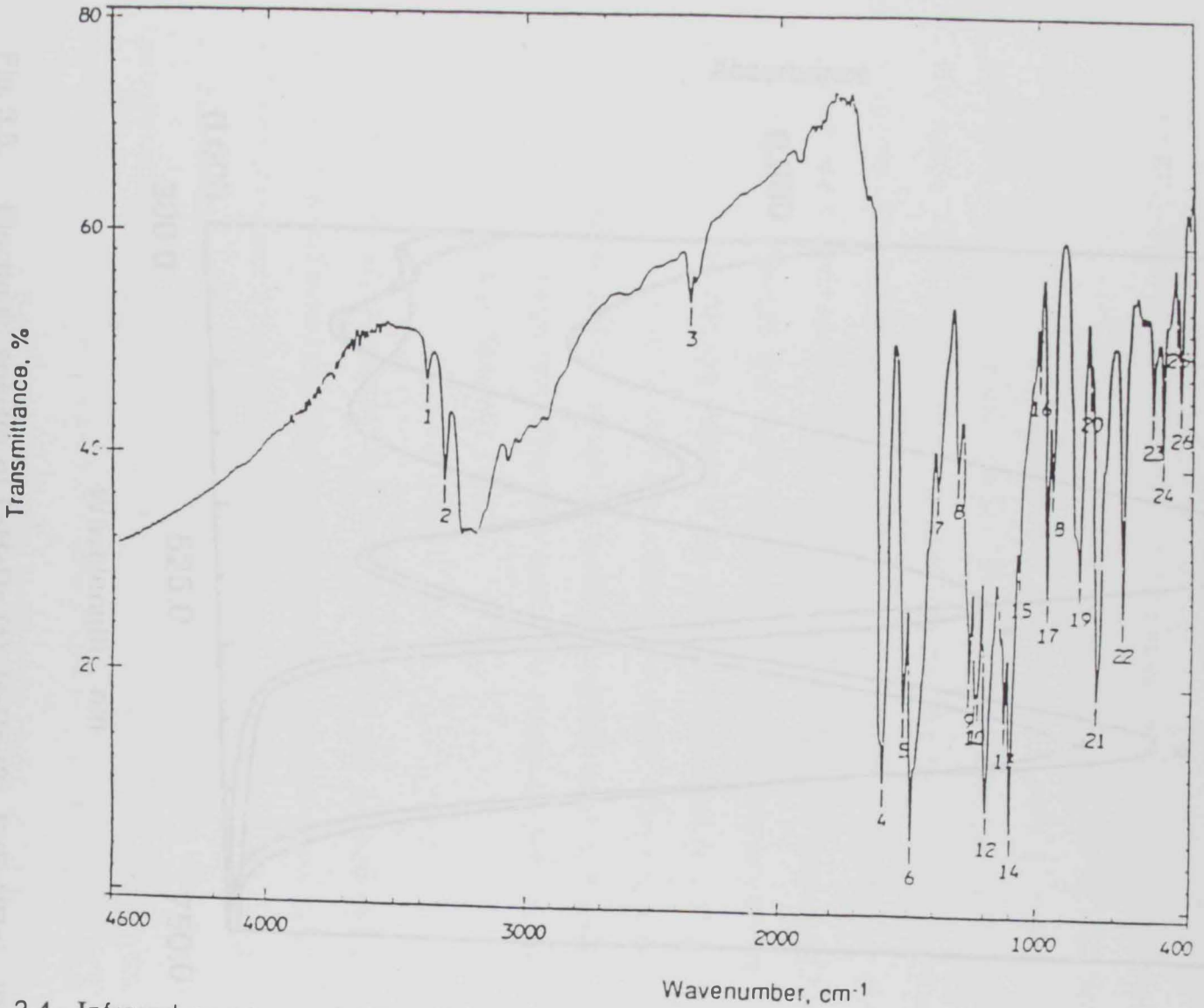


Fig. 3.4. Infrared spectrum of 1,5-di-phenyl-3-mercaptoformazan (H_2Dz) in potassium bromide desk.

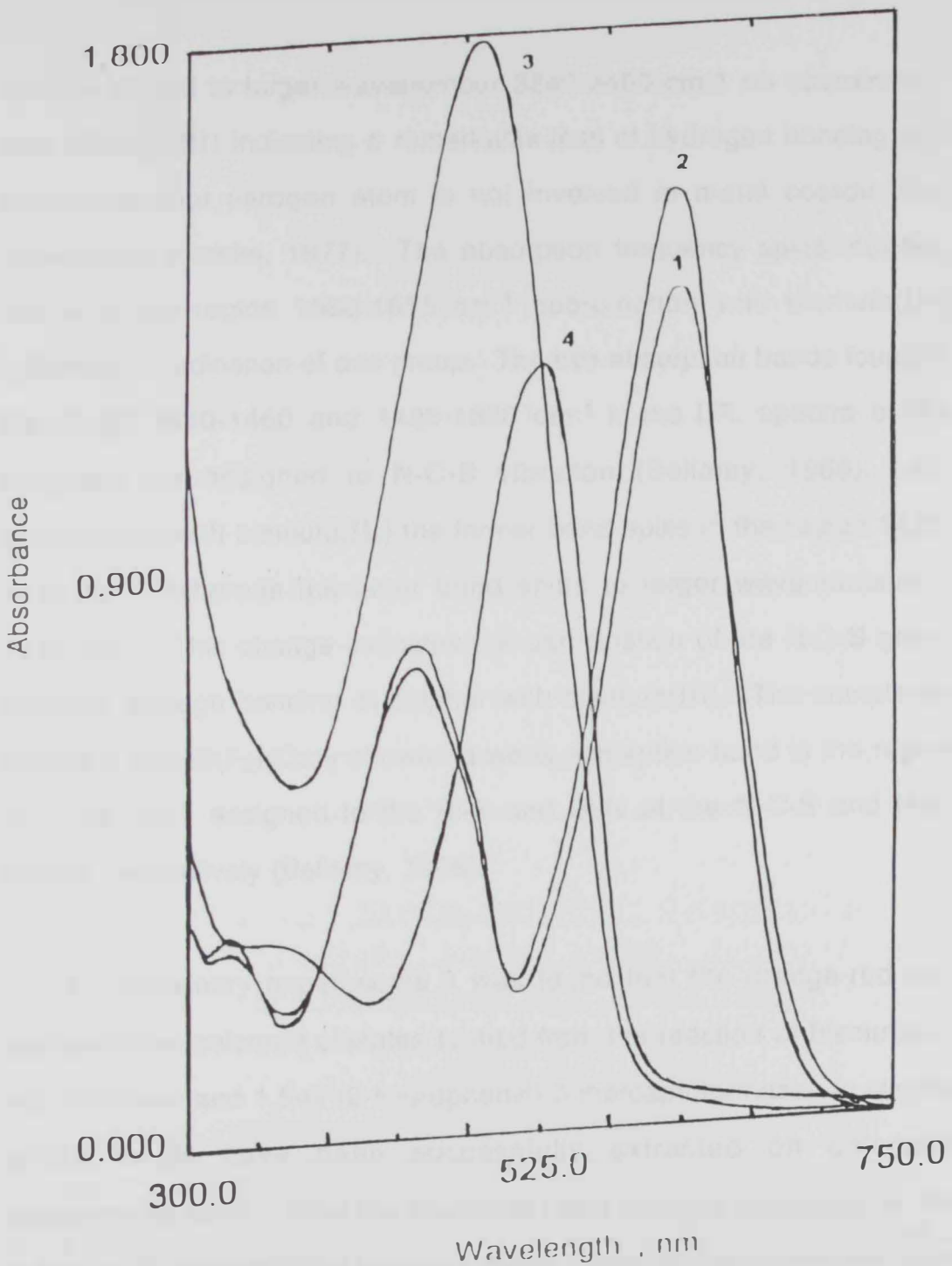


Fig. 3.5. Electronic spectra of F_2H_2Dz (1), H_2Dz (2), $Bi(F_2HDz)_3$ (3) and $Bi(HDz)_3$ (4) in dichloromethane.

band is shifted to larger wavenumber 3240-3460 cm-1 on coordination with bismuth(III) indicating a remarkable loss of hydrogen bonding and suggesting that nitrogen atom is not involved in metal coordination (Kiwan and Kassim, 1977). The absorption frequency splits into two bands in the region 1580-1655 cm^{-1} coordination with bismuth(III) indicating coordination of azo group. The two absorption bands found in the range 1440-1460 and 1420-1520 cm^{-1} in the I.R. spectra of the reagents are assigned to N-C-S vibration (Bellamy, 1968). On coordination with bismuth(III) the former band splits in the region 1430-1470 cm^{-1}, whereas the latter band shifts to larger wavenumbers > 1530 cm^{-1}. This change indicates the participation of the N-C-S group probably through bonding of sulphur with bismuth(III). The complexes $Bi(HDz)_3$ and $Bi(F_2HDz)_3$ showed a weak absorption band in the region 715-730 cm^{-1} assigned to the Bi-S and Bi-N of the N-C-S and N=N groups, respectively (Bellamy, 1968).

In preliminary experiments it was found that the orange-red and orange-brown coloured chelates formed from the reaction of bismuth(III) with dithizone and 1,5-di-(2-fluorophenyl)-3-mercaptoformazan in slightly acidic media have been successfully extracted on unloaded polyurethane foam. Thus the analytical utility of these reactions for the detection of bismuth(III) in aqueous media employing polyurethane foam was tried. Immobilized polyurethane foam with H_2Dz or F_2H_2Dz or plasticized with these reagents in the presence of tri-n-butylphosphate as

a plasticizer was found suitable for the sensitive and selective detection of bismuth(III) in aqueous solution using static (batch), dynamic (column) and pulsating column techniques. Evidently the quasispherical membrane structure, the favourable hydrodynamic and aerodynamic, resilience and mechanical properties of the polyurethane foam facilitate its use in the preconcentration and collection of traces amounts of bismuth(III) on these surfaces. The immobilization of hydrophobic organic extractants e.g. dithizone and 1,5-di(2-fluorophenyl)-3-mercaptoformazan on solid foams (chromofoams) combines the advantages of liquid-liquid and liquid-solid extraction step which is usually much more advantageous with respect to phase separation. Also, the possibility of using loaded solids in a multistage column extraction experiments allows the isolation and concentration of the analyte from the matrix yielding an appropriate enrichment.

3.3.1. Qualitative and Semiquantitative Determination of Bismuth(III) in Aqueous Media Using Unloaded and Polyurethane Foam Immobilized and Plasticized with 1,5-Di(2-fluorophenyl)-3-mercaptoformazan:

3.3.1.1. Batch experiments: On shaking one cube of the unloaded foam with 3-5 cm^3 of the test bismuth solution $Bi(F_2HDz)_3$ in a test tube at pH , 4 for 2-3 min it was possible to detect bismuth(III) at a concentration as low as 0.02 ppm. The colour of the foam cube changed from colourless (blank) to orange-red. The sensitivity of the test can significantly be improved by immobilizing the foam cubes with the

reagent F_2H_2Dz. On shaking one cube of the reagent F_2H_2Dz-loaded foam and plasticized F_2H_2Dz-TBP foam with 2-3 cm^3 of bismuth(III) present at low concentration in the aqueous media as low as 0.01 and 0.005 ppm were easily detected, respectively. The relatively high available surface area of the foam cube acts as an efficient collector for bismuth(III) present in the aqueous solution at low concentration. This, together with the ease of observing the characteristic red colour of the reaction product on the thin membranes of the foam material. In the plasticized F_2H_2Dz-TBP foam the colour was developed rapidly and lower detection limit was obtained. The non-volatile tributylphosphate play a dual purpose (El-Shahawi, 1994) where it acts as an efficient non-volatile solvent for the reagent F_2H_2Dz as well as plasticizer for the plastic foam itself. This could increase the permeability of the foam material which will enhance the rate of sorption of bismuth(III) ions from the aqueous solution or the plasticized reagent foam. Obviously, a comparison between these results and those reported using the usual spot test (Feigl and Anger, 1972) and that reported by Hamza *et al.*, 1990 employing dithizone loaded foam shows that the F_2H_2Dz-loaded foam method and plasticized F_2H_2Dz-TBP-foam are much more advantages. The plasticized F_2H_2Dz-TBP loaded foams gave the most sensitive results.

A further attractive application of the proposed foam test is its application for the semiquantitative determination of bismuth(III) in

acidic aqueous solution (pH ≤ 5) as the colour density on the foam cube was found directly proportional to the concentration of bismuth(III) in the aqueous solution. Thus, semiquantitative determination of bismuth(III) was found possible by comparison of the colour of the foam cubes with standards prepared from bismuth(III) ions in aqueous acidic solutions at the same experimental conditions. The following colour scale 0.05, 0.1, 1, 5 and 10 ppm of bismuth(III) was successfully employed using the immobilized F_2H_2Dz-loaded foam while the colour scale 0.01, 0.05, 0.1, 1, 5 and 10 ppm was found suitable with 1,5-di(2-fluorophenyl)-3-mercaptoformazan plasticized on the polyurethane foam in the presence of tri-n-butylphosphate as plasticizer.

3.3.1.2. Column flow experiments: The proposed F_2H_2Dz-loaded foam and plasticized F_2H_2Dz-TBP foam are easily packed in columns having good hydrodynamic properties. The foam beds were found suitable for the detection and semiquantitative determination of bismuth(III) present in extremely dilute aqueous solution at present reasonable flow rates. Detection at the ppb level is easily possible by percolating relatively large volumes (0.1-3 dm^3) of the aqueous bismuth(III) solution through the reagent foam column at a reasonable flow rate 2-3 cm^3/min..

In this multistage column sorption process, a series of successive equilibrations between the bismuth(III) ion in the aqueous solution (mobile phase) and the organic reagent F_2H_2Dz- on/in the foam support

is generally considered to have a considerable advantage over liquid-liquid or liquid-solid extraction processes. The collection of low concentrations of metal ions from high volumes of aqueous solution up to the observable sensitivity limit of the colour reaction through the proposed reagent foam columns could be carried out.

The immobilized and plasticized F_2H_2Dz- enhance the sensitivity of the detection limit of metal ions in extremely dilute solutions. This was achieved by passing 1 dm^3 of the test bismuth(III) solution through foam columns packed with 0.2 g F_2H_2Dz-loaded or plasticized F_2H_2Dz-TBP foam at reasonable flow rate (3-5 cm^3 min^{-1}). As low as 10 ppb of bismuth(III) in aqueous solution was easily detected.

In the proposed foam column methods the length of the coloured zone produced from the reaction of the collected bismuth(III) ions and the reagent F_2H_2Dz- or F_2H_2Dz-TBP was directly proportional to the bismuth(III) ions in the aqueous solution. Thus semiquantitative determination of bismuth(III) at extremely dilute solution was found possible. Columns packed with 0.2 g F_2H_2Dz- or F_2H_2Dz-TBP were used for the semiquantitative determination of bismuth(III) using a colour scale covering the concentration range 1 to 50 ppb. Figure 3.6 shows the standard colour scale on the F_2H_2Dz-loaded foam columns. This was achieved by measuring the length of the coloured foam colour zone on the columns after percolating of the test solutions.

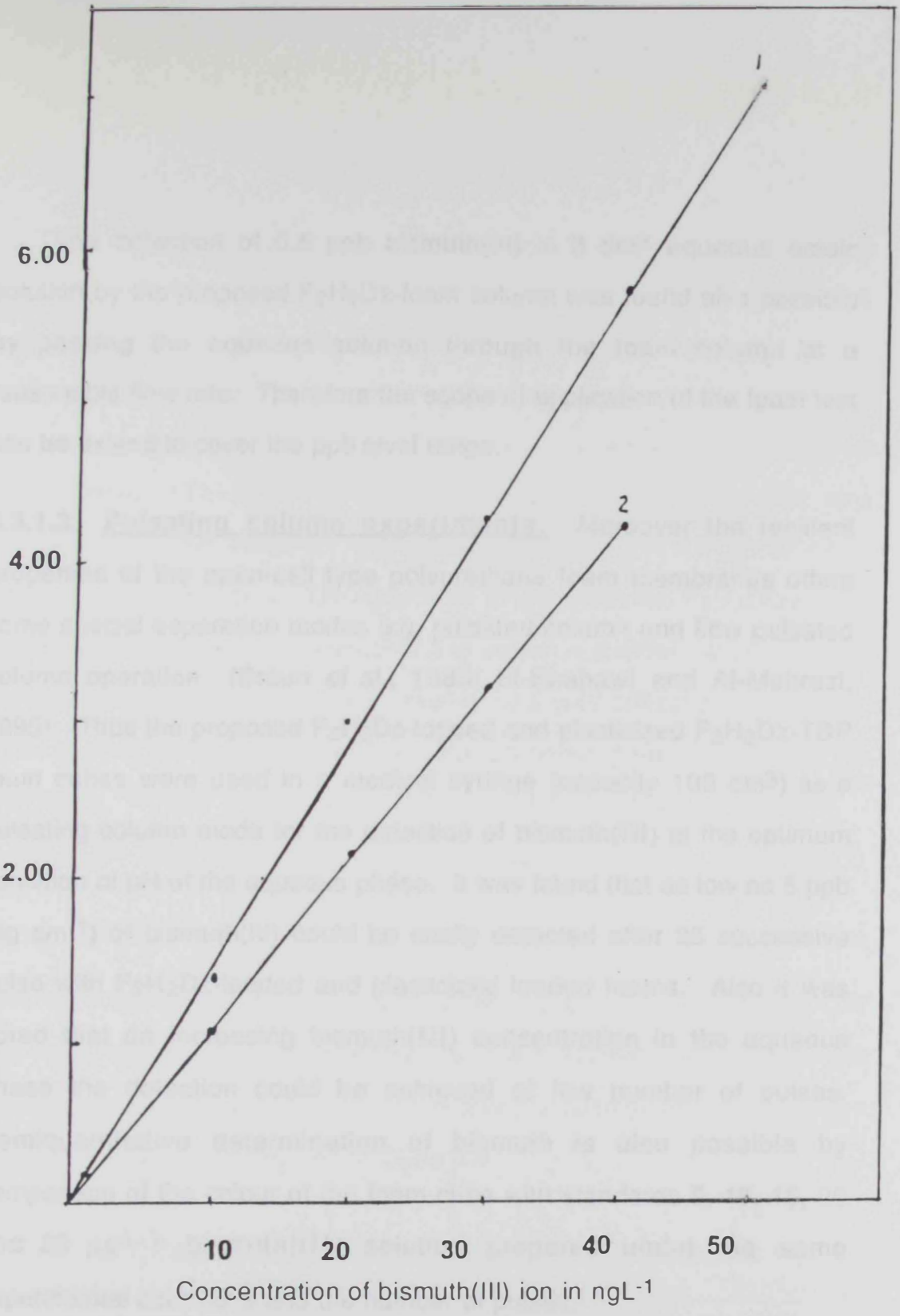


Fig. 3.6. Relationship between the length of the coloured zone (cm) on the foam column and the concentration of bismuth(III) in ng cm^{-3} employing the chromogenic reagents F_2H_2Dz (1) and H_2Dz (2).

The detection of 0.5 ppb bismuth(III) in 3 dm^3 aqueous acidic solution by the proposed F_2H_2Dz-foam column was found also possible by passing the aqueous solution through the foam column at a reasonable flow rate. Therefore the scope of application of the foam test can be extend to cover the ppb level range.

3.3.1.3. Pulsating column experiments: Moreover the resilient properties of the open-cell type polyurethane foam membranes offers some special separation modes e.g. pulsated column and flow pulsated column operation (Braun *et al.*, 1985; El-Shahawi and Al-Mehrezi, 1995). Thus the proposed F_2H_2Dz-loaded and plasticized F_2H_2Dz-TBP foam cubes were used in a medical syringe (capacity 100 cm^3) as a pulsating column mode for the detection of bismuth(III) at the optimum condition of pH of the aqueous phase. It was found that as low as 5 ppb (ng cm^{-1}) of bismuth(III) could be easily detected after 25 successive pulse with F_2H_2Dz-loaded and plasticized loaded foams. Also it was noted that on increasing bismuth(III) concentration in the aqueous phase the detection could be achieved at few number of pulses. Semiquantitative determination of bismuth is also possible by comparison of the colour of the foam cube with standards 5, 10, 15, 20 and 25 μg^{L-1} bismuth(III) solution prepared under the same experimental conditions and the number of pulses.

3.3.1.4. Interference study: The reagent F_2H_2Dz- is not selective and many metal ions including bismuth(III) react with this chelating agent producing different colour species in liquid-liquid extraction. Removal of such interference on the sensitive detection of bismuth(III) in water employing the F_2H_2Dz-loaded foam is considered to be of prime importance. Thus, the practical usefulness of the foam test was examined by the detection of 1 μg of bismuth(III) in the presence of various interfering ions. The selectivity of the proposed F_2H_2Dz-loaded foam on the detection of bismuth(III) in aqueous solution by batch mode of extraction in the presence of diverse ions was critically investigated. The detection of 1 μg of bismuth in the presence of up to 10 mg of the following ions: Li^+, Ca^{2+}, Ba^{2+}, Mg^{2+}, Sr^{2+}, Al^{3+}, NH_4^+, Na^+, K^+, Co^{2+}, La^{3+}, Ga^{3+}, So_4^{2-}, F^-, HPo_4^{2-}, So_4^{2-}, $S_2o_8^{2-}$, No_3^-, Br^-, Cl^-, Vo_3^-, Wo_4^{2-}, So_3^{2-}, Bro_3^-, acetate, citrate, tartrate and ascorbate, was achieved easily. The results obtained are summarized in Tables 3.2 and 3.3. In the presence of some other ions which interfere with the proposed method, a simple modification of the sample solution afforded unambiguous and sensitive detection of bismuth as given in Table 3.4.

3.3.3. Qualitative and Semiquantitative Determination of Bismuth(III) with Immobilized and Plasticized Dithizone-Tributylphosphate Foam

In aqueous acidic solution bismuth(III) reacts with dithizone to form an orange-brown coloured complex. This reaction was employed for the

Table 3.2. Effect of different cations on the detection of 1 µg bismuth(III) by F_2H_2Dz-loaded foam.

Foreign ion	Added compound	Colour of the foam*	Amount of the foreign ion ** (mg)	Bismuth(III) foreign ion
La(III)	$La(NO_3)_3.6H_2O$	White	10	1: 1x 10^4
Co(III)	$CoCl_2.6H_2O$	White-Violet	0.001	1:1 x 10
Ba(III)	$BaCl_2$	White	10	1:1 x 10^4
Ca(II)	$CaCl_2$	White	10	1:1 x 10^4
Sr(II)	$SrCl_2.6H_2O$	White	10	1:1 x 10^4
Mg(II)	$MgSO_4$	White	10	1;1 x 10^4
NH_4^+	NH_4Cl	White	10	1:1 x 10^4
Na^+	NaCl	White	10	1:1 x 10^4
K^+	KCl	White	10	1:1 x 10^4
Li	LiCl	White	10	1:1 x 10^4
Al(III)	$KAl(SO_4)_2.12H_2O$	White	10	1:1 x 10^4
Ga(III)	$GaCl_3$	White	0.1	1:1 x 10^3
As(III)	$NaAsO_2$	White	10	1:1 x 10^4

* The foam colour of the blank test, i.e. in the absence of bismuth(III).

** The amount of foreign ion below which the detection of 1 µg bismuth(III) can easily be achieved.

Table 3.3. Effect of various anions on the detection 1 μg of bismuth(III) by F_2H_2Dz-loaded foam.

Foreign ion	Added compound	Colour of the foam*	Amount of the foreign ion ** (mg)	Bismuth(III) foreign ion
Acetate	CH_3COONa	White	10	$1: 1x\ 10^4$
Tartarate	$KHC_4H_4O_6$	White	0.001	1:1 x 10
F^-	NaF	White	10	$1:1 \times 10^4$
HPO_4^{2-}	Na_2HPO_4	White	10	$1:1 \times 10^4$
SO_3^{2-}	$Na_2SO_3.5H_2O$	White	10	$1:1 \times 10^4$
$S_2O_8^{2-}$	$K_2S_2O_8$	White	10	$1;1 \times 10^4$
WO_4^{2-}	$Na_2WO_4.2H_2O$	White	10	$1:1 \times 10^4$
BrO_3	$KBrO_3$	White	0.1	$1:1 \times 10^2$
SO_4^{2-}	Na_2SO_4	White	10	$1:1 \times 10^4$

* The foam colour of the blank test, i.e. in the absence of bismuth(III).

** The amount of foreign ion below which the detection of 1 μg bismuth(III) can easily be achieved.

Note: In case of metal ions which interfere by their own colours in solution, it was found better to take out the foam cube (after shaking with the test solution) and shake it with 5-10 cm^3 of water.

Table 3.4. Detection of 1 μg bismuth(III) with 1,5-di-(2-fluorophenyl)-3-mercaptoformazan in the presence of some interfering ions.

Foreign ions	Added Compound	Tolerance Limit	Note
Cd^{2+}	$CdBr_2$	1:1 x 10^4	Add few crystals of sodium shlphite
Fe^{3+}	$FeCl_3$	1:1 x 10^4	Add 1 ml of NaF (1M)
Ni^{2+}	$NiCl_2.4H_2O$	1:1 x 10^3	Add few drops of KCN (1M)
Au^{3+}	$AuCl_3$	1:1 x 10^3	Add few crystal of sodium sulphite and adjust pH $\simeq$ 1
MnO_4^-	$KMnO_4$	1:1 x 10^3	Add one crystal of sodium azide
Mn^{2+}	$MnSO_4$	1:1 x 10^4	Add bromine water and boil the solution
Pd^{2+}	$Pd(NO_3)_2$	1:1 x 10^3	Add one crystal of NaF or thiourea
Cr^{3+}	$CrCl_3.6H_2O$	1:1 x 10^3	Add H_2O_2 and boil the solution
Zn^{2+}	$ZnSO_4$	1:1 x 10^3	Adjust pH < 2 of the aqueous solution with HNO_3 (1M)
Oxalate	$H_2C_2O_4.2H_2O$	1:1 x 10^3	Add bromine water and boil the solution
VO_3^-	NH_4VO_3	1:1 x 10^3	Add 1 ml of NaF (1M)
$S_2O_3^{2-}$	$Na_2S_2O_3$	1:1 x 10^3	Add bromine water and boil the solution

detection of bismuth(III) in aqueous solution using polyurethane foam. Polyurethane foams loaded with H_2Dz and plasticized H_2Dz-TBP foams have been employed for the detection of bismuth(III) in extremely dilute aqueous solutions via batch and column modes of extraction. As low as 0.02 ppm bismuth(III) was easily detected by shaking one cube of H_2Dz-loaded foam or plasticized H_2Dz-TBP foams with 3-5 ml of the test solution in a test tube. These data are in good agreement with that reported by Hamza *et al.*, 1990. In the case of the plasticized foam the coloured complex was developed rapidly on the relatively high surface area of the foam. The tributylphosphate increase the permeability of the foam which will enhance the rate of sorption of the complex $Bi(HDz)_3$ from the aqueous solution. The semiquantitative determination of bismuth(III) in aqueous solution was also achieved by a comparison of the colour of the plasticized H_2Dz-TBP foam cubes with a standard colour scale ranging from 0.02-10 ppm bismuth(III) solutions under the same experimental conditions.

The proposed H_2Dz-loaded and plasticized H_2Dz-TBP foams were also employed in column mode for the detection of bismuth(III) at smaller amounts ($\leq$ 0.01 ppm). It was found that as low as 1 ppb of bismuth(III) could easily be detected in aqueous solution by percolating 250 ml of the test solution through the foam column at 2-3 $cm^3\ min^{-1}$ flow rate. The length of the coloured zone in the case of the plasticized H_2Dz-foam was found proportional to the bismuth(III) concentration (Fig. 3.6).

Therefore, semiquantitative determination of bismuth is also possible using standard colour scale ranging from 1-40 ng ml^{-1}.

Obviously, the results obtained with 1,5-di(2-fluorophenyl)-3-mercaptoformazan are much better than that obtained by dithizone. The higher acidity of F_2H_2Dz (pK_a = 4.05) and the relatively higher stability constant of its bismuth(III) complex (log k_{ex} = 11.49) compared to dithizone (pk_a = 4.7) and its bismuth(III) complex (log k_{ex} = 9.75) may partially account for this behaviour (Kiwan and Kassim, 1977). The diffusion rates of $Bi(F_2HDz)_3$ and $Bi(HDz)_3$ through the thin membrane of the polyurethane foam may also pay significant roles in the preconcentration step by the foam.

CHAPTER 4

CONCLUSION

4.1. CONCLUSION

Unloaded polyether based polyurethane foam in batch and column modes can be applied to trap trace amounts of some pyrethroid and phosphorous insecticides from aqueous media. The sorption profiles of Malathion and Parathion in the presence of alkali metal ions were consistent with the solvent extraction mechanism, while the retention behaviour of Cypermethrin and Chloropyrifos were indicative of a cation-chelation mechanism. Studies on the extraction of the tested insecticides by the untreated foam illustrated the importance of the extraction media and the molecular weight of the sorbate.

The study of the tested compounds shows that some of the insecticides are extracted in their neutral form by a simple solvent-extraction mechanism. This conclusion is supported by the short time required for the extraction equilibrium and the salting-out phenomenon. Separation of the tested species can be achieved provided that there is a sufficiently large difference in the optimum condition of extraction of each compound. Open cell type resilient polyurethane foams exhibits excellent hydrodynamic properties which permit their utilization in rapid separation in column mode operations at relatively high flow rate without significant impairment of the separation efficiency. Moreover, the foam offers a wide range of modifications than normal granular solids. The good hydrodynamic properties of the foam sorbent give unique advantage in rapid, versatile and preconcentration of the tested compounds.

The results of plant analysis showed a significant effect of Chloropyrifos on the dry and wet weight of Tomato and Parsley plant leaves. A significant effect on the nitrogen content and trace metals (P, Na, K, Zn, Cu, Mn and Fe) was also achieved on comparison of the controlled and uncontrolled Parsley and Tomato treated with Chloropyrifos for periods of 24, 72 and 120 hrs.

The resilient open-cell type polyurethane foam membranes represent a new type of cheap and efficient separation and preconcentration medium with steadily versatile application in inorganic species analysis. The immobilization of the F_2H_2Dz- or H_2Dz on polyurethane foam extends the application of the foam on the sensitive, selective detection and semiquantitative determination of bismuth(III) in extremely dilute aqueous solution by comparison of the colour scale of the foam cubes with standards prepared under the same experimental conditions. Removal of the interference of the diverse ions on the detection of bismuth(III) in water by the proposed procedure is of prime importance. It seems that polyurethane foam membranes with firmly anchored functional group could offer new horizons in separation science and technology.

REFERENCES

4.2. REFERENCES

Adamson, A.D. (1967). "Physical Chemistry for Surfaces". 2nd Ed., Academic Press, N.Y.

Afghan, B.K., R.J. Wilkinson, A. Chow and T.W. Findey (1984). "A Comparative Study of the Concentration of Polynuclear Aromatic Hydrocarbons by Open Cell Polyurethane Foams". Water Res., Vol. 18 (1), 9-16.

Al-Fassi and C.M. Wai (1992). "Preconcentration Techniques for Trace Elements". CRC Press, Fl. Boca Raton.

Anjaneyulu, Y., R. Marayy and T.H. Rao (1993). "Studies on Thio-Substituted Polyurethane Foam(T-PUF) as a New Efficient Separation Medium for the Removal of Inorganic/Organic Mercury from Industrial Effluents and Solid Wastes". Environmental Pollution Vol. 79, 283-291.

Argekar, A.M. and A.K. Shetty (1995). "Extraction and Spectrophotometric Determination of Bismuth(III) with Cyanex". Analyst, Vol. 120, pp. 1819-1822.

Bellamy, L.J. (1968). "Advances in Infrared Group Frequencies", Methuen, P. 357.

Beltyukova, S.V., Nazarenko, N.A. and Tsygankova, S. (1995). "Sorption of Yttrium Hydroxiquinolinates by Polyurethane Foam and its Use in Rock Analysis". Analyst 120 (6), 1693-1698.

Bowen, H.J.M. (1970). "Adsorption by Polyurethane Foam: A New Method of Separation". J. Chem. Soc., Vol. A, pp. 1082-1085.

Bowen, H.J.M. (1971). "Use of Polyurethane Foams in Extraction of Substances from Fluid Media". Radiochem. Radioanal. Lett., Vol. 7, pp. 71.

Braun, T. and A.B. Farag (1972a). "Foam Chromatography, Solid Foams as Supports in Column Chromatography". Talanta, Vol. 19, pp. 828.

Braun, T. and A.B. Farag (1972b). "Reversed-Phase Chromatography, Separation of Palladium, Bismuth and Nickel in Tri-n-butyl-Phosphate-Thiourea-Perchloride Acid System". Anal. Chim. Acta., Vol. 61, pp. 265.

Braun, T., A.B. Farag and A. Klimes-Szmik (1973a). "Reversed-Phase Foam Chromatography, Redox Reactions on Open-Cell Polyurethane Foam Columns Supporting Tetrachloro-hydroquinone", Anal. Chim. Acta., Vol. 64(1), pp. 71-76.

Braun, T., E. Huszar and L. Bakos (1973b). Reversed-Phase Foam Chromatography, Separation of Trace Amounts of Cobalt from Nickel in the Tri-n-octylamine-hydrochloric Acid System". Anal Chim. Acta., Vol. 64 (1), pp. 77-84.

Braun, T. and A.B. Farag (1973). "Reversed-Phase Foam Chromatography, Chemical Enrichment and Separation of Gold in the Tri-n-byutyl-Phosphate-Thiourea Perchloric Acid System". Anal. Chim. Acta., Vol. 65 (1), pp. 115-126.

Braun, T. and A.B. Farag (1973a). "Pulsed Column Redox Techniques with Flexible Foam Filling". Anal. Chim. Acta, Vol. 65 (1), pp. 139-145.

Braun, T. and A.B. Farag (1973b). "Recovery of Gold from Thiourea Solutions with Open-Cell Polyurethane Foam". Anal. Chim. Acta, Vol. 66 (3), pp. 419-426.

Braun, T. and A.B. Farag (1974a). "Chromofoams Qualitative and Semiquantitative Tests with Chromogenic Organic Reagents Immobilized in Plasticized Open-Cell Polyurethane Foam". Anal. Chim. Acta., Vol. 73 (2), pp. 301-309.

Braun, T. and A.B. Farag (1974b). "Ion Exchange Foam Chromatography, Rapid Separation on Heterogeneous Cation Exchange Foams". Anal. Chim. Acta., Vol. 68 (1), pp. 119-130.

Braun, T. and A.B. Farag (1974c). "Plasticized Open-Cell Polyurethane Foam as a Universal Matrix for Organic Reagents in Trace Elements Preconcentration Collection of Silver Traces on Dithizone Foam". Anal. Chim. Acta, Vol. 69 (1), pp. 85-96.

Braun, T. and A.B. Farag (1974d). "Static and Dynamic Redox Exchange Separations on Finally Divided Copper Immobilized in Open Cell Polyurethane Foam". Radiochem. Radioanal. Lett., Vol. 19 (5-6), pp. 377-388.

Braun, T. and A.B. Farag (1975a). "Cellular and Foamed Plastics as Separation Media. New Geometrical Foam of Solid in Analytical Liquid-Solid Contact". Talanta, Vol. 22 (9), pp. 699-705.

Braun, T. and A.B. Farag (1975b). "Plasticized Open-Cell Polyurethane Foam as a Universal material for Organic Reagents in Trace Element Preconcentration Collection of Cobalt Traces on 1-nitroso, 2-naphthol and diethylammoniumdithiocarbamate Foams". Anal. Chim. Acta, Vol. 76 (1), pp. 107-112.

Braun, T. and A.B. Farag (1975c). "Static and Dynamic Isotope Exchange Separation on Hydrophobic Organic Phases Immobilized Open-Cell Polyurethane Foams". J. Radioanal. Nucl. Chem., Vol. 25 (1), pp.5-16.

Braun, T. and A.B. Farag (1975d) in T. Braun and G. Ghersini (Eds.). "Use of Cellular Plastics in Extraction Chromatography", Elsevier, Amsterdam and Akademiai Kiado, Budapest. pp. 344-365.

Braun, T. and A.B. Farag (1978a). "Polyurethane Foam of the Polyether Type as a Solid Polymetric Extractant for Cobalt and Iron from Thiocyanate Media". Anal. Chim. Acta., Vol. 98 (1), pp. 133-136.

Braun, T. and A.B. Farag (197b). "Polyurethane Foams and Microspheres in Analytical Chemistry, Improved Liquid-Solid Contact Via a New Geometry of the Solid Phase. Anal. Chim Acta, Vol. 99, p.p. 1-36.

Braun, T., J.D. Navrartil and A.B. Farag (1985). "Polyurethane Foam Sorbents in Separation Science". CRC Press Inc., FL, Boca Raton.

Bruland, K.W. (1983). "Trace Elements in Sea-Water". Chem. Oceanogr., Vol. 8, 187-188.

Caletka, R., R. Hausbeck and V. Kirvan (1985). "Extraction of Molybdenum, Tungsten and Technetium with Polyurethane Foam and with Cyclic Polyether from Thiocyanate/Hydrochloric Acid Medium". Fresenius J. Anal. Chem., Vol. 320, pp. 665.

Caletka, R., R. Hausbeck and V. Kirvan (1986). "Extraction of Molybdenum, Tungsten and Technetium with Polyurethane Foam and with Cyclic Polyether from Thiocyanate Hydrochloric Acid Medium". Talanta, Vol. 33 (4), pp. 315-320.

Canadian Drinking Water Limits (1968). "Canadian Drinking Water Standards and Objectives". Department of National Health and Welfare, 1969.

Carvalho, M.S., J.A. Medeiros, A.W. Nobrega, J.L. Mantovano and V.P.A. Rocha (1995). "Direct Determination of Gallium on Polyurethane Foam by X-Ray Fluorescence". Talanta, Vol. 42 (1), pp. 45-47.

Chakraborti, N., and S.K. Roy (1993). "Extraction of Manganese(II) with Dithizone and Potassium Thiocyanate on Foam Sorbents for Spectrophotometric Determination in Silicates". Talanta, Vol. 40 (10), pp. 1499-1503.

Chapman, H.D. and P. Pratt (1961). "Methods of Analysis for Soils, Plants and Waters". University of California, Division of Agricultural Sciences.

Chow, A., W. Branagh and J. Chance (1990). "Sorption of Organic Dyes by Polyurethane". Talanta, Vol. 37 (4), pp. 407-412.

Chow, A.S.Y., B.K. Afghan, J.W. Rubinson (1982). "Analysis of Pesticides in Water, Significant Principles, Techniques and Chemistry of Pesticides". CRC Press Inc., Boca Raton, Vil. 1.

Corbett, J.R. (1974). "The Biochemical Mode of Action of Pesticides". Academic Press, London, New York.

David, D.J. and H.B. Staley (1969). "Analytical Chemistry of the Polyurethanes". Vol. 16, Part 3, John Wiley and Sons, New York.

Edward, C.A. (1973a). "Persistent Pesticides in the Environment". CRC Press, Boca Raton, FL, 2nd Ed., pp. 160.

Edward, C.A. (1973b). "Pesticides Residues in Soil and Water in Environmental Pollution by Pesticides". Ed. Plenum Press, New York, pp. 409.

El-Nabarawy, Th. and L. Bolous (1987). "Activated Carbons in Minimizing Water Pollution". Bull. NRC, Egypt, Vol. 12, 53-70.

El-Shahawi, M.S. (1994). "Retention and Separation of Some Organic Water Pollutants with Unloaded and Tri-n-Octylamine Loaded Polyester-Based Polyurethane Foams". Talanta, Vol. 41 (9), pp. 1481-1488.

El-Shahawi, M.S., A.B. Farag and M.R. Mostafa (1995). "Preconcentration and Separation of Phenols from Water by Polyurethane Foams". Sep. Sci. and Tech. Vol 29 (2), pp. 289-299.

El-Shahawi, M.S., A.M. Kiwan, S.M. Aldhaheri and M.H. Saleh (1994). "The Retention Behaviour and Separation of Some Water Soluble Organophosphorous Insecticides on Polyester-Based Polyurethane Foams". Talanta, Vol.42, pp. 1471-1478.

El-Shahawi, M.S. and M.M. Kamal (1995). "Microgram Determination of Bismuth by Sequential High Fold Chemical Amplification Reactions". Anal. Sci. (Japan) , Vol. 11, pp. 323-327.

El-Shahawi, M.S. and S.M. Aldhaheri (1995). "Preconcentration and Separation of Acaricides by Polyether Based Polyurethane Foam". Anal. Chim. Acta (Galley Proof).

El-Shahawi, M.S. and R.S. Mehrezi (1995). "Detection and Semiquantitative Determination of Bismuth(III) in Water on Immobilized-and Plasticized-Poyurethane Foams with Some Chromogenic Reagents". Submitted for Publication, Talanta.

Emmerling, G., K.H. Schaller and H. Valentin (1986). "Actual Knowledge on Antimony, Bismuth and Other Metals, and their Compounds and Feasibility of Quantitative Determination in Biological Materials in Occupational Medicine and Toxicology" (in German). Zentralvl. Arbeitsmed. Vol. 36, pp. 258-265.

Farag, A.B., A.M. El-Wakil and M.S. El-Shahawi (1981). "Qualitative and Semiquantitative Determination of Chromium(VI) in Aqueous Solution Using 1,5-Diphenylcarbazide-Loaded Foam". Analyst (London), Vol. 106, pp. 809-812.

Farag, A.B., A.M. El-Wakil and M.S. El-Shahawi (1982a). "Detection and Semiquantitative Determination of Nickel with Dimethylglyoxime-Loaded Foam". Talanta, Vol. 29 (9), pp. 789-790.

Farag, A.B., A.M. El-Wakil and M.S. El-Shahawi (1982b). "Qualitative and Semiquantitative Determination of Ion(III) in Aqueous Thiocyanate Solution Using Tricaprlrylamine-Foam". Ann. Chim. (Rome), Vol. 72 (1-2), pp. 103-106.

Farag, A.B., A.M. El-Wakil and M.S. El-Shahawi (1985). "Separation of Cadmium(II), Iron(III), Nickel(II) and Copper(II) in Aqueous Solutions Using Adogen-FoamColumns". Bull. Soc. Chim. Belg., Vol. 94 (9), pp. 631-633.

Farag, A.B., M.A. Morsi and S.A. Ibrahim (1986). "Sensitive Detection and Semiquantitative Determination of Copper and Palladium in Aqueous Solution Using Biacetylmonoxime Benzolhydrazone Loaded Foam". Indian J. Chem., Sect., Vol. A (9), pp. 882-883.

Farag, A.B., A.M. El-Wakil and M.S. El-Shahawi (1986). "Collection and Separation of Some Organic Insecticides on Polyurethane Foam Columns". Fresenius J. Anal. Chem., Vol. 324, pp. 59.

Farag, A.B., M.E.M. Hassouna and M.H. Abdel-Rahman (1987). "Sensitive Detection and Semiquantitative Determination of Mercury(II) in Aqueous Solution Using Dithizone-Loaded Polyurethane Foam". Bull. Soc. Chim. Belg., Vol. 96(2), pp. 147-148.

Farag, A.B., A.M. El-Wakil, M.S. El-Shahawi and M.A. Mashaly (1989a). "Extraction and Recovery of Some Organic Insecticides on Polyurethane Columns". Anal. Sci. (Japan), Vol. 5, pp. 415.

Farag, A.B. A.M.A. Helmy, M.S. El-Shahawi and S. Farrag (1989b). "Sensitive Detection and Semiquantitative Determination of Molybdenum Using Unloaded and Specially Treated Polyurethane Foam". Analusis, Vol. 17 (8), pp. 478-480.

Farag, A.B. and M.S. El-Shahawi (1990). "A Comparative Study on the Extraction, Recovery Chromatographic Separation of Some Organic Insecticides Using Unloaded Polyurethane Foam Column". A paper accepted for publication in the Inter. Symp. Chromatogr., Holland, Sept. 23-28.

Farag, A.B. and M.S. El-Shahawi (1991). "Removal of Organic Pollutants from Aqueous Solution, Comparative Study of the Extraction, Recovery and Chromatographic Separation of Some Organic Insecticides Using Unloaded Polyurethane Foam Columns", Journal of Chromatography, Vol. 552, (1-2), pp. 371-379.

Farag, A.B. and E.M. El-Nemma (1992). "Detection and Semiquantitative Determination of Cobalt(II) and Mercury(II) in Aqueous Media Using Polyurethane Foam Treated with 1-(2-Pyridylazo)-2-Naphthol (PAN)". Int. J. of Chemistry, Vol. 3, (2), pp. 81-88.

Farag, A.B., M.S. El-Shahawi and S. Farrag (1994). "The Sorption Behaviour and Separation of Some Metal Thiocyanate Complexes on Polyether-Based Polyurethane Foam", Talanta, Vol. 41 (4), pp. 617-623.

Feigl, F. (1950). "Spot Tests in Organic Analysis". Elsevier, Amsterdam, 6th ed.

Feigl, F. and A. Anger (1972). Spot Tests in Inorganic Analysis". Elsevier, Amsterdam, 6th ed.

Fong, P. and A. Chow (1992a). "Extraction of Alkylammonium Tetraphenylborates and Dipicrylaminates by Polyurethane Foam". Anal. Chim. Acta, Vol. 260 (1)., pp. 123-130.

Fong, P. and A. Chow (1992b). "Extraction of Alkali-Metal Tetraphenylborates by Polyurethane Foam". Sep. Sci. and Tech. Vol. 27 (10), pp. 1291-1305.

Fong, P. and A. Chow (1992c). "Extraction Mechanism of Monovalent Ion-Pairs by Polyurethane Foams". Talanta, Vol. 39(7), pp. 825-836.

Fong, P. and A. Chow (1992d). "Extraction of Aromatic-Acids and Phenols by Polyurethane Foam". Talanta, Vol. 39 (5), pp. 497-503.

Gesser, H.D., A. Chow, F.C. Davis, J.F. Uthe and J. Reinke (1971). "Extraction and Recovery of Polychlorinated Biphenyls (PCB) Using Porous Polyurethane Foam". Anal. Lett. Vol. 4 (12), pp. 883-886.

Gesser, H.D., E. Bock, W.G. Baldwin, A. Chow, D.W. McBride and .W. Lipinsky (1976). "Open-Cell Polyurethane Foam Sponge as a "Solvent Extractor for Gallium and Iron". Sep. Sci., Vol. 11 (4), pp. 317-325.

Gesser, H.D. and S. Ahmed (1990). "The Extraction of Uranium from Acidic Solutions by Adogen Imprignated Open Cell Polyurethane Foam Sponge". J. Radioanal. Nucl. Chem., Vol. 140 (2), pp.395-408.

Gross, S. (1969). "Modern Plastics Encyclopedia". 46, McGraw-Hill, New York, pp. 248.

Halmann, M. and D.W. Lee (1980). "Recovery of Nickel from Ammoniacal Media with Dimethylglyoxime-Loaded Open-Pore Polyurethane Foams". Anal. Chim. Acta., Vol. 113, pp. 383-387.

Hamza, A.G., A.B. Farag and A. Al-Herthani (1985). "Detection and Semiquantitative Determination of Cadmium and Copper Using Polyurethane Foam Loaded with Selective Reagents". Microchemical J., Vol. 32, 13-17.

Hamza, A.G., A.B. Farag, T.A. Amireh, Z.E. El-Basyouni and F.M. Al-Nowaiser (1990). "Detection, Quantitative Collection and Semiquantitative Determination of Bismuth(III) in Aqueous Media Using Polyurethane Foam Treated with Dithizone". Anal. Sci., 6, 889-891.

Hunter, B.A. and M.J. Kleinfied (1966). "Low Temperature Expansion of Polysulfide Rubbers". Rubber Chem. Technol., 39 (2), 211-216.

Kiwan, A.M. and A. Kassim (1977). "1,5-bis(2-fluorophenyl)-3-mercapto-formazan. A New Metal Extractant". Anal Chim. Acta., Vol. 88, pp. 177-183.

Koch, K.R. and I. Nel (1985). "Immobilization of Platinum(II) in the form of Chloro (trichlorostannate) Platinum(II) Anions by Polyurethane Foams". Analyst (London), 110 (2), 217-218.

Lal, D. J.R. Arnold and B.L.K. Somayajulu (1964). "Method for Extraction of Trace Elements from Sea-Water". Geochim. Cosmochim. Acta, Vol. 28 (7), 283-291.

Lewis, R.G., A.R. Brown and M.D. Jackson (1979). "Evaluation of Polyurethane Foam Sampling of Pesticides, Polychlorinated Biphenyls and Polychlorinated Naphthalene in Ambient Air". Anal. Chem., Vol. 49 (12), pp. 1668.

Lo, V.S.K. and A. Chow (1979). "The Extraction of Antimony with Open-Cell Polyurethane Foam". A. Anal. Chim. Acta, Vol. 106, Iss (1), pp. 161-165.

Lo, V.S.K. and A. Chow (1981). "Extraction of Tin by the Use of Polyurethane Foam". Talanta, Vol. 28 (3), pp. 157-160.

Moody, G.J. and J.D.R. Thomas (1982). "Chromatographic Separation and Extraction with Foamed Plastics and Rubbers". Marcel Dekker, Inc.

Navratil, J.D. and R.E. Eievers (1977). "Air Sparge Batch Contactor for Solvent Extraction Processing of Mixed Actinide Residues". Chem. Separ., Vol. 38, pp. 126-132.

Nerin, C., M. Martinez, B. Pons and J. Cacho (1993). "Behaviour of Solid Absorbents for the Sampling of Atmospheric Organochlorine Compounds". Talanta, Vol. 40 (11), pp. 1769-1774.

Oylet, A.R., D.L. Bodenner, K.J. Welch, R.J. Lukkonen, R.M. Carlson, H.L. Kopperman and R. Caple (1978). "Determination of Aqueous Chlorination Reaction Products of Polynuclear Aromatic Hydrocarbon by Reverse Phase High Performance Liquid Chromatography Gas Chromatography". Anal. Chem. Vol. 50, pp. 837.

Palagyi, S. and T. Braun (1992). "Unloaded Polyether Type Polyurethane Foams as Solid Extractions for Trace Elements". J. Radioanal. Nucl. Chem.,. Vol. 163 (1), pp. 69-79.

Palagyi, S., T. Braun, Z. Homonnay and A. Vertes (1992). "Mossbauer Spectroscopic Investigation of the Sorption of Iron by Polyether-Type Polyurethane-Foam Sorbents". Analyst, Vol. 117 (10), pp. 1537-1541.

Palagyi, S. and T. Braun (1994). "Transport Extraction for Trace-Element Separation and Preconcentration. Polyurethane Foam Sorbent Supported Transport Extraction". Fresenius J. of Anal. Chem., Vol. 348 (3), pp. 211-214.

Schiller, P. and G.B. Cook (1971). "Determination of Trace Amounts of Gold in Natural Sweet Waters by Nondestructive Activation Analysis After Preconcentration". Anal. Chim. Acta, Vol. 54, pp. 364-368.

Schroreder, S.G. and A. Chow (1992). "Polyurethane Foam Extraction of Platinum in Halide Complexes". Talanta, Vol. 39 (7), pp. 837-847.

Schumack, L. and A. Chow (1987). "Extraction of Aromatic Organic Compounds by Polyurethane Foams". Talanta, Vol. 34 (11), pp. 957-962.

Stewart, I.I. and A. Chow (1992). "The Separation of Tellurium and Selenium by Polyurethane Foam Sorbents". Talanta, Vol. 40 (9), pp. 1345-1352.

Sukiman, S. (1974). "Extraction of Gold from Aqueous Solution with Treated and Untreated Polyurethane Foams". Radiochem. Radioanal. Lett., Vol. 18, pp. 129-134.

Thomas, C.R. (1965). "The Formation of Cellular Plastics". British Plastics, pp. 552.

Tyagi. R.D. (1992). "Performance of RBC Coupled to a Polyurethane Foam to Biodegrade Petroleum Refinery Waste Water". Environment Pollut., Vol. 76, pp. 61.

U.S. Drinking Water Limits (1962). "Public Health Drinking Water Standards". U.S. Department of Health, Education and Welfare, Public Health Services.

Weisz, H. (1970). "Microanalysis by the Ring Oven Technique", Pergamon Press, Oxford, 2nd ed.

West, R.C. (1973). "Handbook of Chemistry and Physics". 54th ed., CRC Press.

Valente, I. and H.J.M. Bowen (1977). "A Method for concentrating Antimony from Natural Waters". Anal. Chim. Acta, Vol. 90 (1), pp. 315-318.

ARABIC SUMMARY

و H_2Dz فى التقدير شبة الكمى لايون البزموت الموجود فى المحاليل المائية بتركيزات ضئيلة جدا .

ب- فى سلسلة التجارب الديناميكية أمكن الكشف عن تركيزات من ايون البزموت الثلاثى الموجود بتركيزات فى حدود ٥ جزء من البليون من الجرام بواسطة البلاستيك الرغوى المحمل بواسطة المرتبط F_2H_2Dz كما امكن استخدام هذة الطريقة فى التقدير شبة الكمى الميكرونى لايونات البزموت الموجود بتركيزات ضئيلة فى المحاليل المائية .

ج- وطبقا لخاصية المرونة الموجودة فى عديد اليورثيان امكن استخدام الاعمدة النبضية المعبأه بعديد اليوريثان المحمل بالمركب المخلبى ١،٥- ثنائى (٢-فلوروفينيل) - ٣- ميركابتو فورمازان فى الكشف عن تركيزات فى حدود ٥ جزء من البليون من الجرام .

د- امكن ايضا الكشف عن تركيزات فى حدود ١ ميكروجرام من ايونات البزموت الثلاثى الموجودة فى المحاليل المائية فى وجود العديد من الكاتيونات والانيونات المختلفة بواسطة الطرق الاستاتيكية عن طريق استعمال عديد اليورثيان المحمل بالمركب F_2H_2Dz .

تم ايضا حساب المحتوى الحرارى (ΔH^{o}) وعشوائية النظام (ΔS^{o}) لكل مبيد من هذة المبيدات عند استخلاصة بواسطة البلاستيك الرغوى .

ولقد اوضحت الطرق الاستاتيكية إمكانية استخدام كروماتوجرافيا العمود فى فصل وتركيز المبيدات المذكورة ولقد امكن حساب عدد (N) وسمك (HETP) الطبقات النظرية للعمود المعبأ بواسطة البلاستيك الرغوى غير المحمل .

تم ايضا تقدير نسب وتركيزات النيتروجين والفوسفور والبوتاسيوم والصوديوم والزنك والنحاس والمنجنيز والحديد و نسبة الرطوبة و الوزن الجاف والوزن الرطب لنبات الطماطم والبقدونس المعالجة وغير المعالجة بمبيد الكلوروبيريفوس عند ازمنة مختلفة من الرش (من صفر -١٢٠ ساعة)

٢- التحليل الوصفي وشبة الكمي الميكروني لأيون البزموت الثلاثي باستخدام البلاستيك الرغوى مفتوح الخلايا :

اوضحت الدراسة إمكانية استخدام المركبات ١، ٥- ثنائى (٢-فلوروفينيل) - ٣- ميركابتو فورمازان H_2F_2Dz وكذلك ١ ، ٥- ثنائى (فنيل) -٣- ميركابتوفورمازان (H_2Dz) فى الكشف الكيفى وشبة الكمى الميكرونى لأيون البزموت الثلاثى فى وسط حمضى (pH <5) بواسطة عديد اليوريثان الرغوى المحمل وغير المحمل بهذه المركبات ولقد اوضحت النتائج الاتى :-

أ- فى سلسلة التجارب الاستاتيكية امكن الكشف عن تركيزات فى حدود ٠,٠٢ ، ٠,٠١ ، ٠,٠٠٥ من المليون من الجرام من ايونات البزموت الثلاثى الموجودة بواسطة عديد اليوريثان غير المحمل والمحمل بواسطة H_2Dz و F_2H_2Dz فى وجود ثلاثى بيوتيل الفوسفات على التوالى .

امكن ايضا الكشف عن تركيزات ٠,٠٢ من أيون البزموت الثلاثى بواسطة عديد اليوريثان المحمل بالمركب H_2Dz كما تم الكشف عن ايونات البزموت الثلاثى الموجوده بتركيز واحد فى المليون من الجرام فى وجود العديد من الكاتيونات والانيونات المختلفة والموجودة بتركيزات عالية . امكن ايضا استخدام هذة المرتبطات F_2H_2Dz

نتائج الدراسة

توصلت هذة الدراسة لمجموعة من النتائج أهمها :-

١-الفصل الكمي لبعض المبيدات الحشرية المختلفة من المحاليل المائية:

تم استخلاص المبيدات الحشرية العضوية الآتية : باراثيون ، مالثيون ، سيبرميسرين والكلوروبيريفوس من المحاليل المائية المختلفة باستخدام الأعمدة الممتلئة بالبولى يوريثان الرغوى غير المحمل ، ووجد أن هذة المبيدات يمكن تجميعها كميا على البلاستيك الرغوى غير المحمل كما يمكن استعادة تلك المبيدات من البولى يوريثان الرغوى ايضا باستخدام جهاز السكسوليت المعبأ بالأسيتون كمذيب ثم قياس تركيز المادة المستخلصة من المبيد بالاستعانة بجهاز الأشعة فوق البنفسجية عند الطول الموجى المناسب لكل مبيد حشرى .

ولقد تم استخدام الطرق الاستاتيكية لدراسة تأثير العوامل المختلفة مثل الوسط والرقم الهيدروجينى ، وتركيز المبيد وكذلك تأثير الكاتيونات المختلفة مثل الليثيوم ،الصوديوم ، والبوتاسيوم والامونيوم ، وكذلك درجة الحرارة على عملية الفصل ومن ثم تم تحديد ميكانيكية استبقاء كل مبيد ولقد اوضحت النتائج الخاصة بمبيد المالثيون والباراثيون ان الاستخلاص يزداد بزيادة تركيز الايون المضاف طبقا للترتيب الاتى :

$$Li^+ > Na^+ > K^+ > NH_4^+$$

وهذا دليل على ان استخلاص هذين المبيدين يتم بواسطة الاستخلاص بالمذيب (Solvent extraction mechanism) و اوضحت الدراسة ايضا ان المبيدين الحشريين سيبرميسرين والكوروبيريفوس يتم استخلاصهما بواسطة ميكانيكية الارتباط الكاتيونى (Cation chelation mechanism) حيث إن الاستخلاص يزداد طبقا للترتيب الاتى :

$$K^+ > NH_4^+ > Na^+ > Li^+$$

الملخص العربي

مقدمة

لا شك ان تطبيق الرغويات عديدة البوريثان المسامية المحملة وغير المحملة بكاشفات عضوية ملونة كمستخلصات فراغية صلبة يعتبر إضافة مفيدة في مجال طرق الفصل الكيميائي والتقدير الوصفي وشبه الكمي لعديد من المركبات والعناصر ، كما أن التركيب الفقاعي وشبة الكمي لرغويات عديدة البوريثان يسهم بمميزات خاصة مثل جمع وتركيز كميات متناهية الصغر على سطحها الكبير ، وداخل ثناياها مما يمكننا من الكشف عنها بسهولة ودقة عالية .

هدف الدراسة :

استهدفت هذة الدراسة مايلي:

١- تقصى إمكانية استخدام عديد البوريثان المحمل وغير المحمل في استبقاء وفصل والتقدير شبه الكمي والكيفي لبعض الملوثات العضوية وغير العضوية من المحاليل المائية المختلفة .

٢- دراسة تأثير مبيد الكلوروبيريفوس على العديد من العناصر المختلفة في نبات الطماطم ونبات البقدونس عند أزمنة مختلفة من التعرض للمبيد .

طريقة الدراسة :

تضمنت هذة الدراسة الفعاليات الاتية :

١- استخدام البلاستيك الرغوى عديد البوريثان في فصل وتقدير العديد من المبيدات الحشرية الفوسفورية مثل مبيد بارائيون ، مالثيون ، سيرميسرين والكلوروبيريفوس الموجودة بتركيزات متناهية الصغر في المحاليل المائية المختلفة وذلك باستخدام الطرق الإستاتيكية والديناميكية.

٢- التحليل الوصفي وشبة الكمي الميكروني لعنصر البزموت الثلاثي الموجود في المحاليل المائية المختلفة والموجود بتركيزات ضئيلة جدا وذلك باستخدام البلاستيك الرغوى المحمل وغير المحمل بمركبات مخلبية مختلفة وذلك بالاستعانة بطرق الفصل الاستاتيكية وكروماجرافيا العمود وكذلك الأعمدة النبضية .

بسم الله الرحمن الرحيم

جامعة الامارات العربية المتحدة

كلية العلوم

قسم الكيمياء

عنوان الرسالة : السلوك الاستبقائى والفصلى لمبيد الكلوروبيريفوس وبعض الملوثات المائية الاخرى بواسطة البلاستيك الرغوى

اسم الباحث : راشد صالح المحرزى

لجنة التحكيم

م	الاسم	الوظيفة
١	د. محمد سرور السعيد الشهاوى	استاذ مساعد الكيمياء التحليلية بكلية العلوم جامعة الامارات العربية المتحدة
٢	أ.د زكريا مصطفى العتـــال	استاذ المبيدات الحشرية وزارة الزراعة والثروة السمكية
٣	أ.د شريف حسين قنديل	استاذ الكيمياء الفيزيائية وعلوم البوليمرات - كلية العلوم- قسم الكيمياء جامعة الامارات العربية المتحدة

تاريخ المناقشة : ١٩٩٦/٢/٢٦ م

توقيعات لجنة الحكم : .....

م	الاسم	التوقيع
١	د. محمد سرور السعيد الشهاوى	
٢	أ.د زكريا مصطفى العتـــال	
٣	أ.د شريف حسين قنديـــل	

عميد كلية العلوم

استاذ دكتور/ عبد الرحمن سلطان السُرهان

بسم الله الرحمن الرحيم

جامعة الامارات العربية المتحدة

كلية العلوم

قسم الكيمياء

عنوان الرسالة : السلوك الاستبقائي والفصلي لمبيد الكلوروبيريفوس وبعض الملوثات المائية الاخرى بواسطة البلاستيك الرغوى

اسم الباحث : راشد صالح المحرزى

المشرفون

م	الاســـم	الوظيفة	التوقيع
١	د. محمد سرور السعيدالشهاوى	استاذ مساعد الكيمياء التحليلية - كلية العلوم جامعة الامارات العربية المتحدة	
٢	أ.د / محمود هاشم عبد القادر	استاذ الكيمياء الفيزيائية - المعهد القومى لابحاث الليزر - جامعة القاهرة جمهورية مصر العربية .	
٣	أ.د محمد قدوس خان	استاذ الكيمياء الحيوية والسموم -قسم الكمياء الحيوية - جامعة ميشيجان الولايات المتحدة الامريكية	
٤	د. سالم مسرى الظاهرى	مدرس الكيمياء التحليلية - كلية العلوم جامعة الامارات العربية المتحدة	

بسم الله الرحمن الرحيم

جامعة الإمارات العربية المتحدة
كلية العلوم
قسم الكيمياء

السلوك الاستبقائي والفصلي لمبيد الكلوروبيريفوس وبعض الملوثات المائية الأخرى بواسطة البلاستيك الرغوي

رسالة مقدمة من الطالب
راشد صالح المعرزي
بكالوريوس في العلوم والآداب (رئيسي أحياء/فرعي كيمياء)
كلية شابمن - كاليفورنيا (١٩٨٥)

إستكمالاً لمتطلبات الحصول على درجة الماجستير في العلوم
(علوم البيئة)

جامعة الإمارات العربية المتحدة
كلية العلوم
يناير ١٩٩٦