CHAPTER 5

FLOW INJECTION ANALYSIS

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5.1 Advent of automation

With the advent of knowledge and progress in science newer modern methods of analysis came into existance. One of the major landmarks in the history of analytical chemistry is the emergence advent of automation. The automatic methods for routine chemical analysis are becoming popular since last three decades. Automation to various degrees is introduced in number of techniques used for analysis.

5.2 Advantages of automation

Some of the advantages of automation are summarised here,

1. Saves considerable manpower.
2. Online analysis helps to control quality of products which are manufactured on large scale.
3. Rapid analysis of large number of samples can be done in minimum time.
4. Brings accuracy in analysis.
5. Reproducibility of the results is achieved.

5.3 Disadvantages of automation

However, automation has following disadvantages also.

1. Less contact with process and chemists resulting into lack of continuous control over situation leading to prevention of some interesting results.
2. Increased risk of sample-result mismatching during frequent checkups.
3. No knowledge of the limitations, as manufacturers overpraise the product and consumers do not take effort to find out the limitations.

4. It narrows its scope particularly in research.

Hence semiautomatic methods are preferred over completely automatic methods.

5.4 Classification of semiautomatic methods

Semiautomatic methods can broadly be divided into two groups.

i) batch analysers

ii) continuous flow analysers

5.4.1 Batch analysers

In a batch analyser each discrete sample is assigned a container, within which it helds through all the steps necessary to perform the analysis. The disadvantages of all batch analysers are that they are mechanically very complex and have many moving parts which may become worn. The sequential discrete analyser with sample cups is a system in which individual samples are transported through a number of stations where manual operations such as pipetting, diluting, reagent addition, mixing, heating, incubation and measurement are mechanised. Thus simulating a manual procedure.

5.4.2 Continuous flow analysers

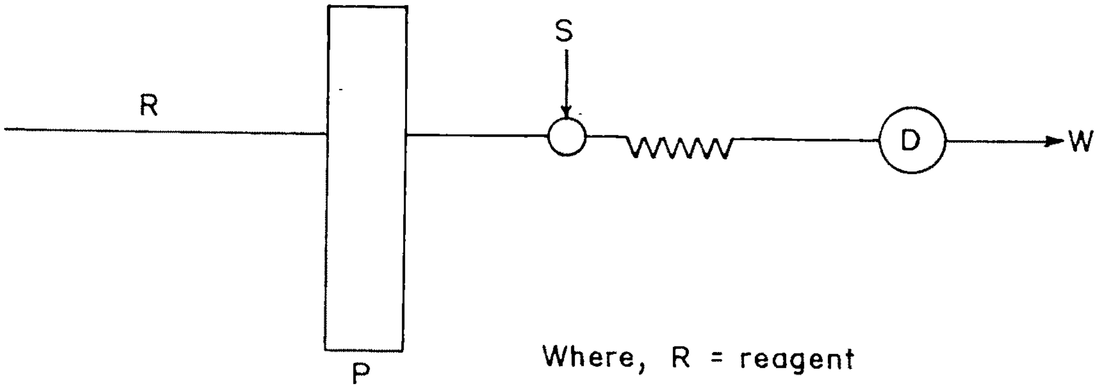
In the broad context continuous flow analysis refers to any process in which the concentration of analyte is measured uninterruptedly in a stream of liquid or gas. In the present context, successive samples pass through the same path in the analyser, reagents being added at strategic points, the mixing and incubation taking place while the sample solution is on its way towards a flow through sample cell, where the signal is continuously monitored and recorded. The greatest difficulty to overcome is to prevent intermixing of adjacent samples during their passage through the analyser conduits. To minimise the intermixing of adjacent samples Skegg[1] introduced air segmentation, thus dividing the flowing stream into a number of compartments separated by air bubbles.

5.5 Comparision of continuous flow and segmented flow analyser

In a continuous flow analyser, a liquid sample is injected into moving, nonsegmented continuous carrier stream of a suitable liquid. The injected sample forms a zone, which is then transported towards a detector which continuously records the signal. Continuous flow injection analyser consists of a pump which is used to propell the carrier stream through a thin tube, an injection port through which a sample solution `S' is injected into the carrier stream in a very reproducible manner and a reaction coil in which sample zone disperses and reacts with the components of the carrier stream forming a species which is sensed by a flow through detector and further recorded.

A typical continuous FIA manifold is shown in Fig. 5.1

Fig. 5·I

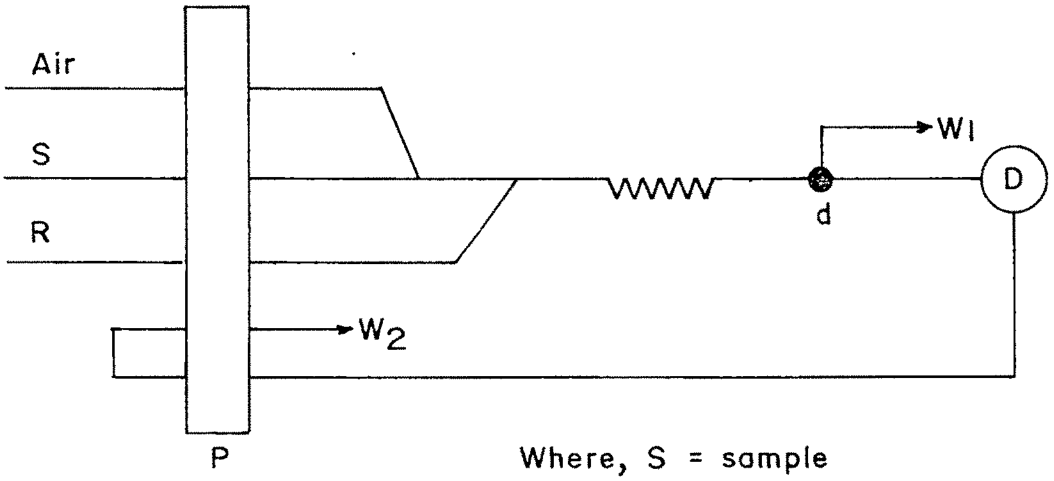


Where, R = reagent
P = peristaltic pump
S = sample injection port
D = detector
W = waste

Whereas in segmented flow analyser the samples are successively aspirated from their individual containers into a tube and then forwarded through a pump into a system, where a flowing stream is regularly segmented by air bubbles delivered by another pump tube. Further downstream a reagent is added to all individual segments which then pass through a reaction coil, where the chemical reaction takes place. Before monitoring the air segmentation has to be removed in a debubbler to avoid a disturbed signal by flow-through detector which is unsuitable for direct recording.

A typical segmented FIA manifold is shown in Fig. 5.2

Fig. 5·2



Where, S = sample
R = reagent
P = peristaltic pump
D = detector
d = debubbler
W_1 & W_2 = waste

5.6 Advantages and disadvantages of continuous flow analysis

Though continuous flow analysis is a versatile technique; it has advantages as well as disadvantages.

Advantages

1. It is a simple and inexpensive technique
2. Versatility of use which affords for developing steps of the analytical process of rather different complexity.
3. Simple use of it enables the high sampling frequency.
4. Reduces the sample and reagent consumption.
5. Possibility of manipulating manifolds in an easy way to develop suitable designs to overcome different short comings.
6. Good reproducibility of the measurements.
7. On-line derivatization reactions, separation processes as well as a number of sample handling modes to fit the initial sample conditions to the most suitable for single and multiple detection of flow through chemical sensors.

Disadvantages

1. Reproducibility of peaks for lower concentrations is good but is poor for higher concentrations.
2. Peak response is sluggish in reaching baseline.
3. Baseline drift may be caused.
4. Formation of air bubbles in carrier stream.
5. Abrupt noise on peaks is observed when air bubbles pass through detector.
6. Movement of the recorder pen may not be smooth. As a result the peaks are recorded in a sawtooth fashion.

7. Negative peaks may arise when the carrier solution is coloured and the injected sample is colourless and very dilute.

5.7 Construction of FIA

Ideal flow injection system should be constructed in such a manner that,

1. The carrier stream flows through a narrow tube of uniform diameter, including the injection and detector sections.
2. The sample solution is injected as an instant pulse of exact volume in a short duration, in such a way that the movement of the carrier stream remains undisturbed.
3. Side streams are added to the main stream in an easily reproducible manner.
4. The flow of all streams is pulse free and that can be started and stopped instantaneously.
5. The detector instantly and selectively should respond to the analyte concentration with maximum signal yield.

The main parts of f.i. manifold represented in Fig. 5.1 are (i) Pump, (ii) injection valve, (iii) reaction coil, connector, (iv) detector (v) recorder

Each part of flow manifold is discussed here in brief:

(i) **Pump** : A peristaltic pump is the most suitable means of propelling the carrier stream in f.i. manifold as it can propell several channels, varying the individual tube diameters, equal or different pumping rates can be obtained. A modern pump has a very small inner hold up volume, permitting rapid start up and short wash out periods. We have used the Gilson mini pulse peristaltic pump

(Model HP4) which has a stepwise regulation of the flow rate and generates a pulse-free flow.

(ii) Injection valve : There are two types of sample injection systems used in FIA.

(a) The syringe injection and

(b) The valve injection

The syringe injection mode approximates the sample pulse, which theoretically has some advantages as to the geometrical form of the injected sample zone. Where as the valve injection mode approximates the sample pulse and is a more practical way of introducing well-reproducible sample volumes into a flowing carrier stream without disturbing its motion. That is why the valve injection has gained wide acceptance for FIA applications. We have also used a valve injection mode for sample introduction.

(iii) Reaction coils and connectors : The reaction coils are made of suitable lengths of tightly wound plastic tubing of uniform internal diameter around a metal rod. The diameter of the metal rod controls the helically mixing pattern and is generally 1 to 1.5 cm. The most frequently used internal tube diameter is 0.5 mm, but 0.75 mm is sometimes used to increase dispersion and 0.3-0.5 mm i.d. is useful when dispersion should be limited. The most suitable tube material is teflon, which besides being chemically resistant, generally is delivered as tubes of highly uniform internal diameters. Polyethylene and polypropylene tubing is inexpensive and easy to flange. It is very important that coils and connecting pieces of tubing be well adhered on a solid support, so that the flow path remains unchanged during each set of experiments.

(iv) **Detectors :** One of the advantages of f.i. technique is its versatility. This is reflected in the wide selection of detectors for the analysis. The types of detecting systems useful in f.i. modes are spectrophotometer, fluorimeter, nephelometer, turbidometer, chemiluminescence, atomic absorption flame photometer, potentiometer and voltameter.

However, the modification is needed in the sample cells. For electrochemical methods, flow cells used are (i) cascade type flow cell and (ii) wire-type flow cell

Whereas the conventional spectrophotometers are provided with low-pressure flow through cells which are available with small hold up volumes and overall dimensions fitting to a large variety of commercial spectrophotometers. We have used a flow through cell having 20 μl volume. In atomic absorption flame photometry no cell is required.

(v) **Recorder :** A recorder is an indispensable component of a well designed system, as it delivers not only the read out, from which the analytical result is obtained, but also records the shape of each peak, which permits even as post diagnosis of errors and yields a permanent record for later retrospective evaluation and retains a legal attestation, if required. A recorder is the most flexible tool for research and investigation of f.i. techniques.

5.8 FIA manifold for preconcentration

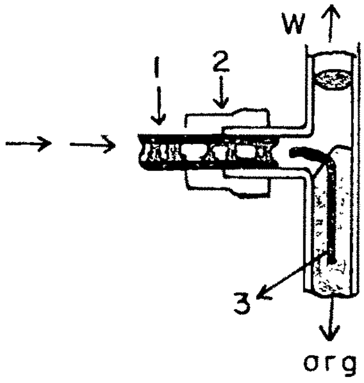
Micro quantities of metal ions can be determined through on-line solvent extraction and ion exchange process in flow system.

5.8.1 On-line solvent extraction method

In this technique, the aqueous sample, a component of which has to be extracted, is injected into an aqueous carrier stream to which the organic phase is continuously added and after passing through the extraction coil, the organic phase is again separated from the aqueous phase and further carried through the flow cell for continuous measurement. In solvent extraction flow system, the separator can be made in a simpler or a more sophisticated version.

The simple separator is made of a standard A4 fitting into which either a teflon fiber or a strip of Whatman IPS phase separating paper is inserted. The organic phase is separated by its adhesion to these hydrophobic materials, and this process is further assisted by differential pumping. So the flow rate of the organic phase can be drawn out. But only 60-80 % organic phase can be removed. Thus some of the organic phase and all the aqueous solution leaves for waste. The simple T separator is shown in Fig. 5.3 (a).

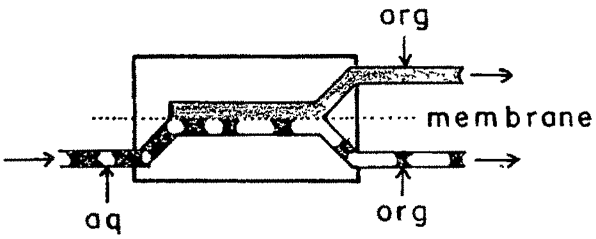
Fig.5·3(a)
T - Separator



1. Teflon tube
2. Elastic sleeve
3. Teflon fibre

In sophisticated separator, a microporous teflon membrane with polyethylene backing as a phase separator is used which is called membrane phase separator (Fig. 5.3 (b)). At flow rates of 0.5 to 1.0 ml/min, this device is capable of separating alcohols, alkanes, chlorinated hydrocarbons and aromatic solvents from the aqueous phase with upto 95 % efficiency.

Fig. 5·3 (b)
Membrane phase separator

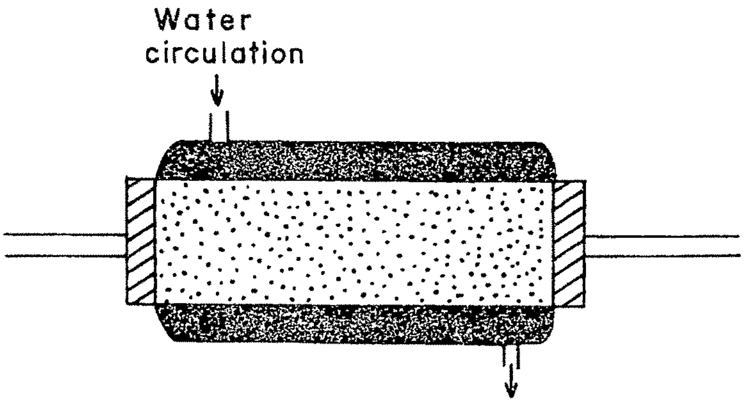


Though this method is effective, it is time consuming, laborious and difficult to perform in the microscale. For a simple and low level estimation after preconcentration, ion exchange column can be introduced in FIA.

5.8.2 On-line ion exchange method

In online exchange in flow system, microcolumns are used by placing an ion exchange material in between glass wool plugs at the two ends of columns and using adhesive for sealing both the ends. By this method nanogram quantities of metal ions can be estimated after preconcentration. Another advantage is that the preconcentration can be done at elevated temperature or at low temperature by circulating water around microcolumn (Fig. 5.4).

Fig.5·4
Microcolumn

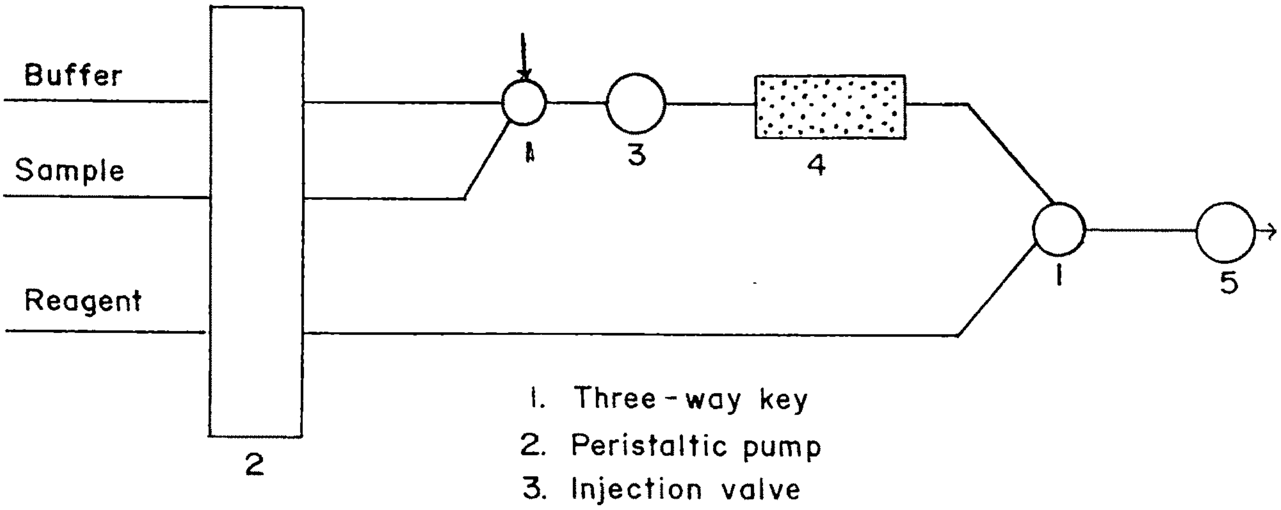


5.9 FIA manifold used in the study

FIA manifold used in the present study was constructed using the components described in the previous section 5.7. In FIA manifold, the detector used was uv-visible spectrophotometer to measure the absorbance/peak height due to formation of coloured complexes. Study of copper (II), nickel (II), zinc (II), cadmium (II), mercury (II), gold (III) and palladium (II) was carried out using FIA manifold with uv-visible spectrophotometer as a detector.

A continuous flow manifold as shown in Fig. 5.5 was constructed for the study of preconcentration of metal ions using micro columns of chelating resin under study. Micro columns of various length and 2 mm i.d. were used by placing chelating resin in between glass wool plug at two ends of columns and using adhesive for sealing both the ends. Gilson minipulse peristaltic pump (model HP4) was used having flow rate regulator. Injection valve (Rheodyne RH 5020) with 20 μl flow cell and uv-visible spectrophotometer was used as detector along with X-t chart

. Fig. 5·5
FIA manifold with uv-visible spectrophotometer



1. Three-way key
2. Peristaltic pump
3. Injection valve
4. Microcolumn containing resin
5. Detector (uv-visible spectrophotometer)

recorder in the manifold. The flow rate was regulated as required and wave length for detection was selected for the particular metal ion. A three way key was used to mix metal solution and reagent without disturbing pulse. A chelated metal ion from the ion exchange micro column was eluted by injecting a 20 µl of eluting agent through fixed volume loop fitted in a six way injection valve.

5.10 Use of micro columns in FIA

One of the greatest advantages of flow injection technology is the ease with which additional components can be added to the system, to achieve a particular analytical objective, without adversely affecting the original analytical measurement. Introduction of a small column of an ion exchange resin into a flow injection manifold could be used in a number of ways as stated below.

(i) For the removal of interferences of metal ions and anions[2].

(ii) To concentrate metal ion from a bulk of very very dilute solution[3-5].

(iii) For separation and estimation of metal ions from the mixtures[6].

(iv) For the determination of one anion by replacement of other anion which is suitable for colourimetric determination[7].

Though the first continuous flow analysis was reported in 1975, online preconcentration using microcolumns was reported first time in 1980 by Kilinghoffer[50]. Gradual increase in the number of publications arising every year shows the importance of the technique. From 1975 to 1986 the publications in this area have shown a steep rise where as after 1990 there is a steady growth.

5.11 Online preconcentration of metals in flow injection analysis

The flow injection analysis, one of the semiautomated methods is marked by the introduction of micro column containing ion exchanger for preconcentration of metal ions in year 1980. There after number of manifolds have been developed for single and double injections as well as split and non-split sample devices for separation and simultaneous detection of metal ions. We have used f.i. manifold (Fig. 5.5) for the online preconcentration of copper, nickel, zinc, mercury, gold and palladium using micro column filled with the dithizone anchored poly (vinyl pyridine) resin and uv-visible spectrophotometer as a detector.

5.12 Experimental

A flow injection manifold as shown in Fig. 5.5 was constructed as described in section 5.9.

5.12.1 Optimisation of experimental conditions

Stock solutions of metal ions under study were prepared and standardised as described in section 2.4. The working solutions were prepared by dilution from the stock solutions as per the requirement.

Reagent solutions were prepared by dissolving required quantity of sodium diethyl dithiocarbamate in deionised water, diphenyl carbazide in ethanol, xylenol orange in deionised water and dithizone in dimethyl formamide (DMF).

Appropriate buffer solutions (acetate buffer and citrate phosphate buffer) of 0.2 M strength were prepared as per the standard procedures.

5.12.1.a Effect of pH

The effect of pH on online preconcentration of metal ions in flow injection system was studied using acetate buffers and citrate phosphate buffers of pH 1-7. Buffer solutions of varying pH were passed through the flow manifold (Fig. 5.5) containing microcolumns of chelating resin, at a flow rate of 2.0 cm^3 min^{-1} to equilibrate the resin column at a required pH. Then 5 cm^3 of 1 μg cm^{-3} metal solution was pumped at a flow rate of 2 cm^3 min^{-1} through the microcolumns followed by the buffer solutions of the same pH to remove the unexchanged metal ions from the column. Metal ions from the column were eluted by injecting 20 μl of eluting reagent of required strength through injection valve. Eluted metal was estimated colourimetrically by using organic reagent which was passed through the another channel of the manifold shown in Fig. 5.5. Absorbance due to coloured complex formed was measured at λ_{max} on uv-visible spectrophotometer. Results were recorded on the x-t chart recorder. From the pH vs peak height plots optimum pH for quantitative uptake of the metal by resin was determined.

5.12.1.b Effect of reagent concentration

In the study of effect of reagent concentration on copper, nickel, zinc, cadmium, mercury, gold and palladium the reagents of different concentrations (varying from 0.2 - 2.0%) were passed through the manifold shown in Fig. 5.5. From the recorded peak heights optimum reagent concentration required for metal complexation was determined.

5.12.1.c Effect of flow rate

A 2.0 cm long and 2 mm i.d. columns in the manifold were equilibrated with the optimum pH buffer for 2-5 min at a flow rate of 2 cm^3 min^{-1}. 5 cm^3 of 1 μg cm^{-3} metal solution was passed through the column in the manifold at a flow rate of 1-5 cm^3 min^{-1}. The metal ions from the column were eluted with 20 μl of appropriate eluting reagent of desired strength. The results obtained were recorded on x-t chart recorder.

5.12.1.d Effect of column length

Microcolumns of different length (1 cm - 4 cm) were used in the flow manifold. 5.0 cm^3 of 1 μg cm^{-3} metal solutions were passed through the column at optimised flow rate and pH. The columns were washed with deionised water and elution of metal from the resin was done by 20 μl of eluting reagent injected through injection valve. The metal was estimated by uv-visible spectrophotometer using appropriate complexing reagent in the 3rd reagent channel of manifold (Fig. 5.5). From the peak height optimum column length was determined.

5.12.1.e Eluting reagents

To achieve the quantitative elution of preconcentrated metal from the resin, various eluting reagents of different strengths were tried by injecting through 20 μl injection loop. The proper eluting reagent was selected by recording the peak heights.

5.12.1.f Calibration plots

Calibration plots for the preconcentration of metal ions in f.i. method were constructed by passing 5 cm^3 of metal solutions of different concentrations through the manifold at optimised conditions followed by the elution of metal from the column with 20 μl eluting reagent. The results were recorded in triplicate. From the peak height obtained on x-t chart recorder calibration plot was obtained as peak height against concentration of metal ion. Regression coefficient for the calibration plots of each metal ion was calculated.

Though batch studies were made for copper, nickel, zinc, lead, cadmium, mercury, gold, platinum and palladium by dividing them into 3 groups, in the online preconcentration studies in continuous flow analysis only copper, nickel, zinc, cadmium, mercury, gold and palladium were examined as we were not able to set the methods properly for platinum and lead. However, particularly in case of lead as $t_{1/2}$ is very large flow system is not desirable.

5.13 Preconcentration of copper, nickel and zinc

Importance of removal and determination of copper, nickel and zinc is already discussed earlier in section 3.4. Here the work done in the online preconcentration of these metal ions in continuous flow analysis is summarized.

5.13.1 Literature survey for online preconcentration of copper, nickel, and zinc using microcolumns.

Flame atomic absorption spectrometry (FAAS) for the determination of copper, nickel and zinc lacks the sensitivity in detection at µg l^{-1} level. Other methods like electrothermal and hydride generation AAS etc are sensitive but suffer from matrix interference. But determination of µg l^{-1} quantities of copper, nickel and zinc through online preconcentration using flow injection technique is most sensitive method and is also free from matrix interferences. So far more than 100 reports are available for the estimation of copper, nickel and zinc by f.i.a. using variety of analytical techniques such as anodic stripping voltametry[8], spectrophotometry[9-12], potentiometry[13], flame atomic absorption spectrometry[14-16], pH metry[17], chemiluminescence[18], amperometry[19], catalytical fluorimetry[20] and so on.

Determination of microquantity of copper through flow injection analysis technique was first time tried by Ruzicka and Hensen[8] in 1978 where as f.i.a. technique for nickel was first tried by Kuroda and Mochizuki[12]. The estimation method for zinc using atomic absorption spectrophotometer was reported first time by Wolf and Stewart[14] in 1979.

Though the f.i.a. methods for estimation are widely used, only a few reports are available for online preconcentration using f.i.a. Our main emphasis being on online preconcentration in f.i.a., we have concentrated here on the works done in online preconcentration using f.i.a.

The first on-line preconcentration in f.i.a using chelex-100 exchanger was reported by Oslen et al[21,22] in 1983 and later in 1988 by Zhang et al[30]. An ion-exchanger immobilised with 8-quinolinol for online preconcentration and determination of copper, nickel and zinc using f.i.a was reported by Malamas et al[22]. Where as Fang et al[23] and Bengtsson and Johansson[24] have reported the use of ion exchanger for preconcentration of nickel using f.i.a. The enrichment factors were reported of the order of 15-20 and 90-100 % recoveries upto 20-50 μg l^{-1} were also reported. Preconcentration and determination of copper at ng level with continuous flow injection analysis has contributed[25,26,28,34] to the development of several semiautomatic methods. Cheng et al[27] developed a method for the estimation of Al (III), Cd (II), Cu (II), Ni (II), Pb (II), Zn (II), Fe (III), Mn (II), Cr (III), Mo (VI), Ti (IV) and V (V) after preconcentration on Chelex-100 in f.i. system. Kashiwabara et al[29] have used a small column packed with immobilised bovine carbonic anhydrase for the determination of traces of zinc in aqueous solution. A linear calibration graph is obtained between $1x10^{-8}$ and $4x10^{-7}$ g of zinc. Chambaz and Haerda[31] used microcolumns containing 8-quinolinol bonded on silica for the preconcentration and simultaneous determination of Cd(II), Cu(II), Ni(II) and Fe(III) at concentration range 10^{-8} to 5×10^{-6} M.

Tsalev et al[32] used an ion exchanger containing tri (pyridyl methyl) ethylene diamine for enrichment of Cu(II), Ni(II), Zn(II), Cd(II) and Pb(II) using f.i.a. Elution of these metals was carried out with HNO_3 and HCl. Inductively coupled plasma detection system was used in flow system by Abollino et al[33], here 8-oxine and its 5-sulphonic acid derivatives immobilised on polystyrene divinyl benzene copolymer were used for the preconcentration at nanogram levels of copper, nickel and zinc. Michael et al[35] have studied online preconcentration and separation of nickel from water samples using electrothermal atomic absorption spectrophotometry. Purohit and Devi[34,36,42] have reported the preconcentration of copper, nickel and zinc using terpolymeric resins containing oxine, resorcinol and different crosslinking agents in flow injection system. Bolei et al[37] have reported the universal chemiluminescence detection using the luminol reaction and the stoichiometric displacement of copper in conjuction with flow injection. Ren et al[38] reported preconcentration of zinc in flow system. Preconcentration and determination of copper and zinc by flow injection analysis are reported by Hiroko and Chizuko[39]. Homogeneous crystalline membranes of silver plate based on conductive epoxy resin for preconcentration of copper using potentiometric detecting device in flow injection system was reported by Isbel et al[40]. Determination of copper in flow injection system after preconcentration using silica based C_{18} support with quinolinol -8-ol, dithizone, sodium diethyldithio carbamate, 1-(2-pyridylazo)-2-naphthol, 4-(2-pyridyl azo) resorcinol was reported by Lancaster et al[41]. They have reported the detection limit using quinolinol-8-ol and sodium diethyl dithiocarbamate at parts -per-billion levels with enhancement factors between 50 and 100. On-line preconcentration of nickel by carbonyl vaporisation with continuous flow systems in combination with sensitive determination by electrothermal, AAS was reported by Erber and Cammann[43]. The detection limit was found to be 0.18 $\mu g\ l^{-1}$. The r.s.d. of this method was lower than 3 %. A brief summary of these methods is given in Table 5.1 for easy referencing.

The chelating resin discussed earlier was used in the form of microcolumn incorporated in a continuous flow system for the preconcentration of copper, nickel and zinc and other metal ions. Various conditions were optimised as discussed earlier in section 5.12.2 for achieving desirable preconcentration levels and quantitative elution and estimation of copper, nickel and zinc.

Table 5.1 : Review of literature survey for online preconcentration of copper, nickel and zinc in flow injection system.

Sr. No.	Ion exchanger or reagent used	Comments	Reference
1	8-Quinolinol on silica gel	Determination of Cu(II) at ng level	21
2	Ion exchanger	Heavy metals from water	21
3	Immobilised 8-quinoline	Enrichment of trace metals	22
4	8-Oxine/ resorcinol / hydroquinon	Conditions optimised for enrichment of Cu(II) at ng level.	34
5	Chelex-100	Al(III), Cd(II), Co(II), Cr(III), Cu(II), Fe (III), Mn(II), Mo(VI), Ni(II), Pb(II), Ti(IV), V(V), Zn(II) from costal and sea water at ng level.	27
6	Chelating resin containing salicylic acid as functional group	Preconcentration of Ni(II) at trace level	23
7	Immobilised bovine carbonic anhydrase	Zn (II) in water,tea,sediments and spring water	29
8	Chelex-100 on silica gel and activated alumina	Determination of Cu(II), Cd(II), Pb(II) and Zn(II) at ppm and ppb levels.	30
9	Tri (pyridyl methyl) ethylene diamine	Enrichment of Cu (II), Cd(II), Ni(II), Pb (II), Co(II), Zn(II), Ca(II), Fe (II) Elution with HNO_3 and Hcl	32
10	8-oxine and 8-oxine 5-sulphonic acid on polystyrene-DVB resin (Amberlite XAD-2)	Ca (II),Cd (II),Cu (II), Mg(II), Mn(II), Ni (II), Pb(II) and Zn(II) with ICP-AES at ng levels	33

11	8-Oxine-resorcinol / hydroquinone/aldehydes	Preconcentration of Zn(II), Cd(II), Cu(II), Ni(II) at ng levels	36,42
12	Strong acidic ion exchanger	Chemiluminescence detection of Cu (II)	37
13	Ion exchange resin	Determination of traces of Zn(II) in hair	38
14	2-(2-Thiazolylazo)-5-(sulfomethyl)amino-p-toluic acid,2- (2-pyridylazo)-1-napthol-4-sulfonic acid etc	For determination of Cu(II), Co(II), Ni (II), Fe(II), U(VI), Ca(II), Ba(II)	39
15	Homogeneous crystalline membrane of metallic silver based on conductive epoxy resin	Cu (II),Cd (II),Pb (II)	40
16	Polymeric hydrophobic sorbent and silica based C_{18} support with quinolinol-8-ol, sodium diethyl dithiocarbamate, 1-(2-pyridyl azo) resorcinol and dithizone reagents	Preconcentration and determination of Cu (II) and Pb(II)	41
17	8-Quinolinol bonded on silica	Determination of Cu (II), Ni(II), Co(II) and Fe (III) using a diode array uv-detecter	31

5.13.2 Results and discussion

Flow injection manifold used for the preconcentration of copper, nickel and zinc is illustrated in Fig.5.5 with a uv-visible spectrophotometer as a detecting device. For the estimation of copper and nickel aqueous solution of sodium diethyl dithio carbamate and for zinc, aqueous solution of xylenol orange was used. Hence in the given manifold channel 1 and 2 were used for the buffer and metal solution respectively and channel 3 for the reagent solution. Care was taken during operation of manifold to avoid mixing of solutions and deposition of reagents on the Walls of the tubing. Periodic cleaning of the system was done. And the system was purged with water thoroughly before closing for a day.

5.13.2.a Effect of pH on preconcentration of copper, nickel and zinc

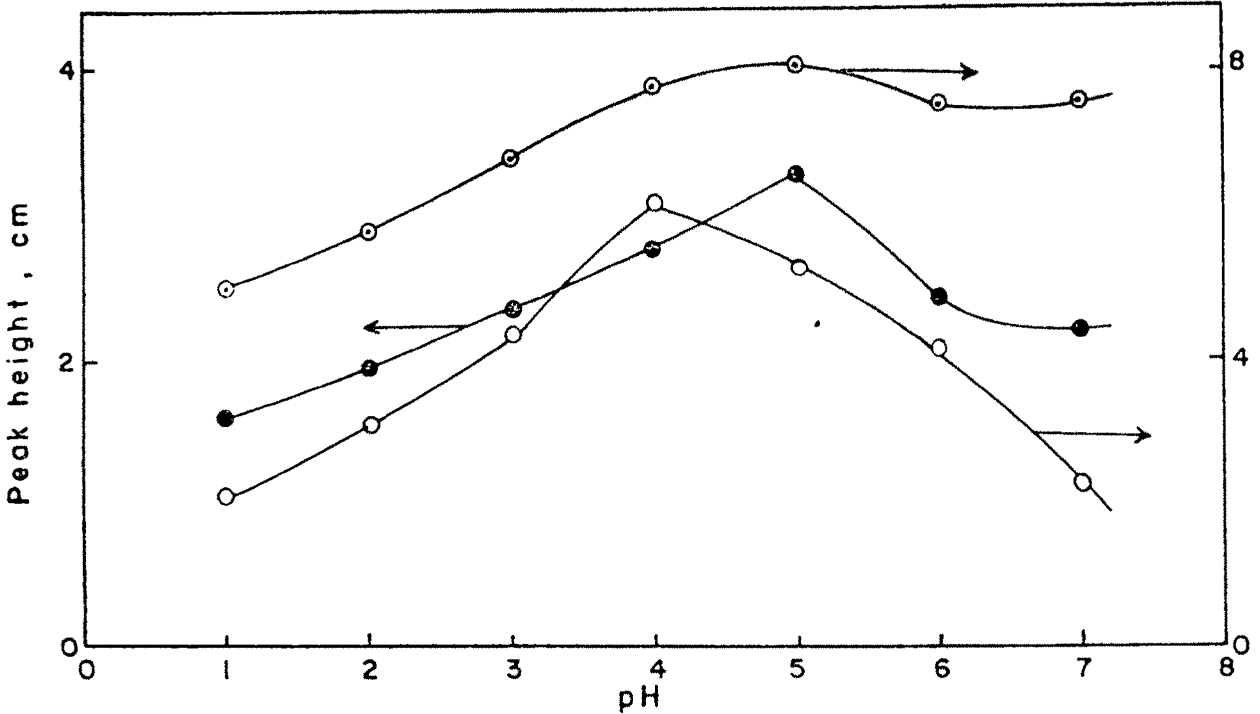
Preconcentration of copper, nickel and zinc was carried out at pH 1-7 using 0.2 M acetate/citrate buffer. Copper, nickel and zinc from the column were eluted by injecting 20 μl of 1.0 M HCl, 2.0 M HCl and 0.5 M HCl respectively. The optimum pH for copper, nickel and zinc was found to be 5, 5 and 4 respectively. The results are given in Fig.5.6. The results obtained in the batch method are observed to be more critical of pH than those in flow system.

5.13.2.b Effect of reagent concentration

In the study of effect of reagent concentration on the estimation of eluted metal it was observed that 0.2 % aqueous solution of sodium diethyl dithiocarbamate for copper and nickel is sufficient and 0.25 % aqueous solution of xylenol orange is sufficient for zinc. The results are given in Fig.5.7.

Fig. 5·6

Effect of pH on preconcentration

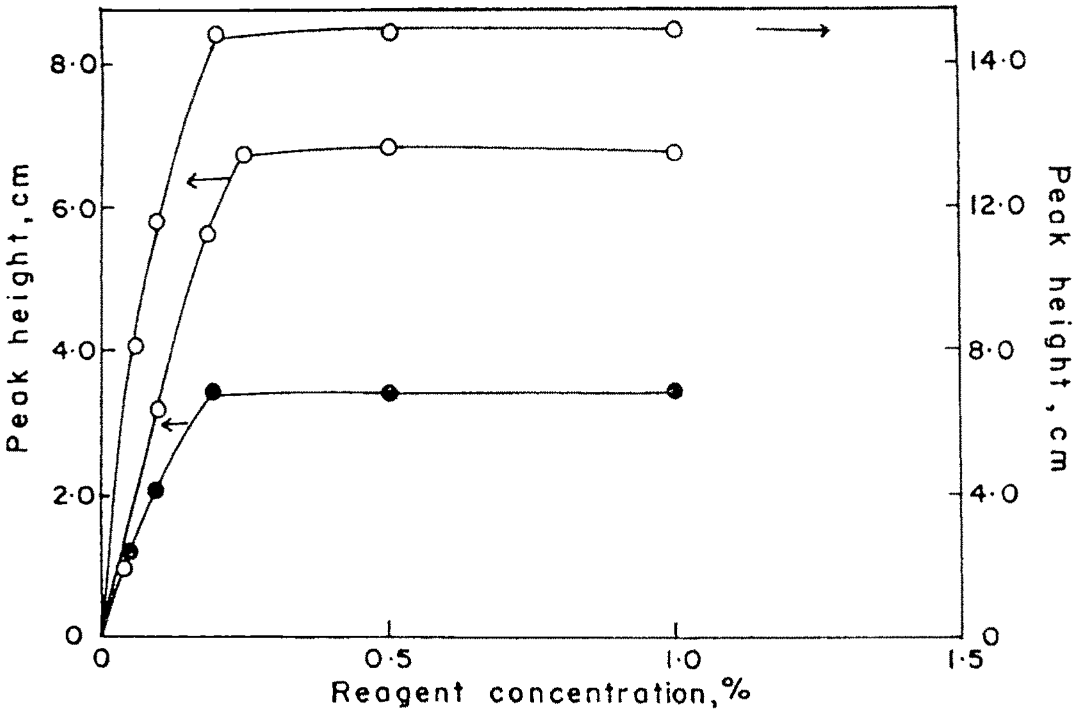


Flow rate 2 cm^3 min^{-1}, metal solution 5 cm^3 of 1 µg cm^{-3}, column length 2 cm , reagent concentration 0·2 – 0·25 % (w/w)

● Copper , ⊙ Nickel , ○ Zinc

Fig. 5·7

Effect of reagent concentration



Optimum pH, metal solution 5 cm^3 of 1 µg cm^{-3}, column length 2 cm, flow rate 2 cm^3 min^{-1}, eluent 20 µl of 0·5 – 2·0 M HCl

● Copper , ⊙ Nickel , ○ Zinc

5.13.2.c Effect of column length

Column length was optimised for each metal under study using 1-4 cm long and 2 mm i.d. glass columns. A 2 cm long column was sufficient for effective preconcentration of copper, nickel and zinc. The results in terms of peak height vs column length are given in Fig.5.8. Further 2.0 cm long column was used throughout the study. Longer column showed increased dispersion particularly in the case of copper and zinc.

5.13.2.d Effect of flow rate

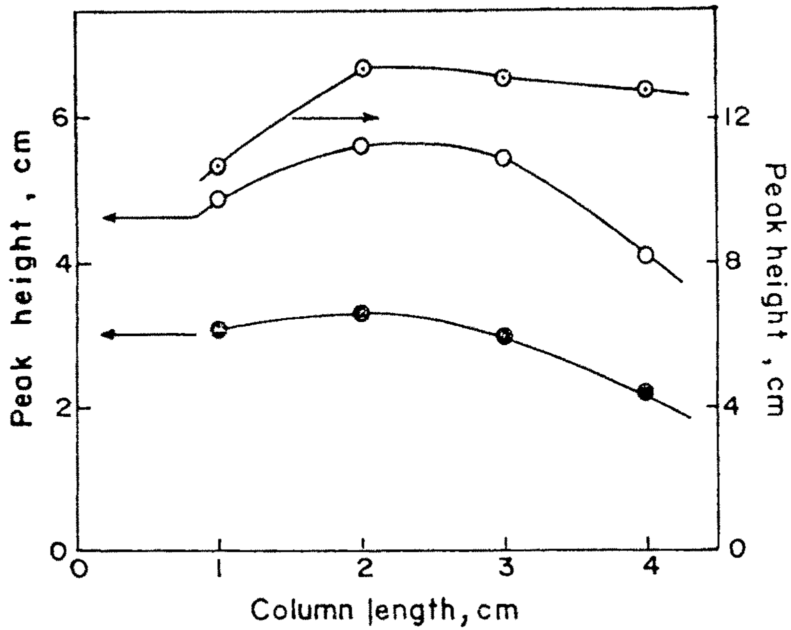
Effect of flow rate on the preconcentration of copper, nickel and zinc was studied by varying the flow rates in the manifold from 1 to 5 cm^3 min^{-1}. It was observed that at lower flow rate, broadening of the peak is considerable where as at higher flow rate, high degree of dispersion is observed resulting into reduced peak height. Results obtained are presented in Fig.5.9. Flow rates of 2-3 cm^3 min^{-1} were observed to be desirable and were used throughout the work.

5.13.2.e Effect of eluting reagent

Elution of preconcentrated metal from the resin under study was done by injecting 20μl of 0.1 to 2.0 M HCl, H_2SO_4, HNO_3, CH_3COOH in the manifold. The observed % elution of the metals is given in Table 5.2. It was observed that 0.5 M - 2.0 M HCl gives quantitative elution of copper, nickel and zinc from the columns under study. Continuous elution of copper using 1.0 M HCl, nickel with 2.0 M HCl and zinc with 0.5 M HCl gives narrow peak of comparable height indicating that the analyte concentration lies in a relatively narrow eluting range. In the flow system

Fig. 5·8

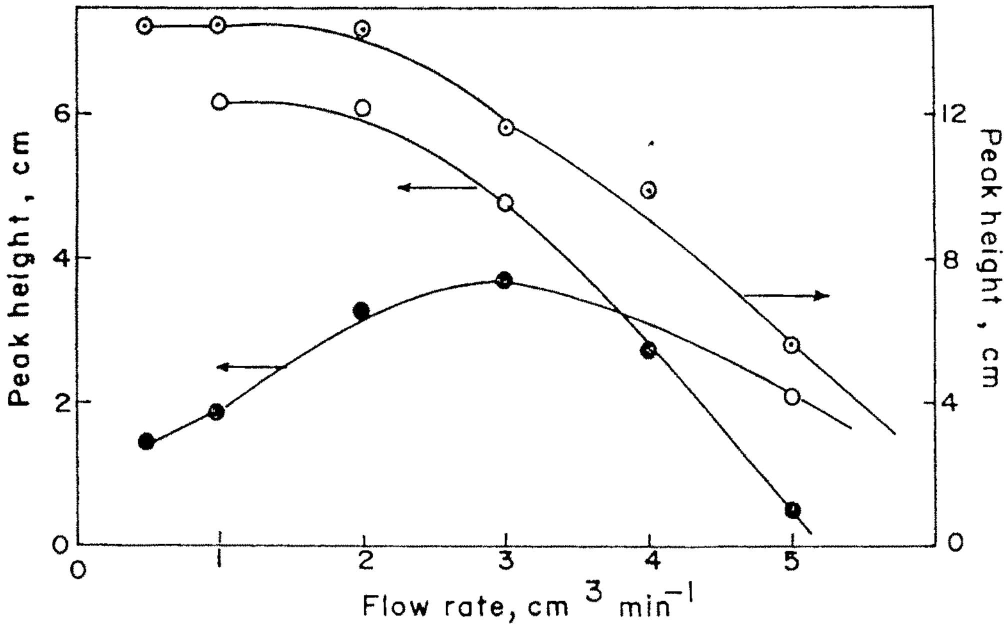
Effect of column length



Flow rate 2 cm^3 min^{-1}, metal solution 5 cm^3 of 1 µg cm^{-3}, optimum pH, eluent 20 µl of 0·5 – 2·0 M HCl
● Copper, ⊙ Nickel, ○ Zinc

Fig. 5·9

Effect of flow rate



Optimum pH, metal solution 5 cm^3 of 1 µg cm^{-3}, column length 2 cm, eluent 20 µl of 0·5 – 2·0 M HCl.
● Copper, ⊙ Nickle, ○ Zinc

Table 5.2 : Study of eluting reagents for copper, nickel and zinc

Optimum pH, flow rate 2 cm^3 min^{-1}, column length 2 cm, metal solution 5 cm^3 of 1 μg cm^{-3}.

Sr. No.	Eluent	% Elution Copper	Nickel	Zinc
1.	M HCl			
	0.1	84.0	63.0	55.0
	0.2	89.0	64.0	69.0
	0.5	92.0	79.0	99.0
	1.0	100.0	87.0	99.0
	2.0	100.0	100.0	100.0
2.	M HNO_3			
	0.1	78.0	14.0	53.0
	0.2	84.0	21.0	71.0
	0.5	89.0	27.0	99.0
	1.0	97.0	29.0	100.0
	2.0	99.0	39.0	100.0
3.	M H_2SO_4			
	0.1	87.0	39.0	62.0
	0.2	90.0	50.0	79.0
	0.5	93.0	56.0	99.0
	1.0	100.0	66.0	100.0
	2.0	100.0	73.0	100.0
4.	M CH_3COOH			
	0.1	00	37.0	69.0
	0.2	00	53.0	73.0
	0.5	00	64.0	80.0
	1.0	00	84.0	99.0
	2.0	00	90.0	100.0

comparatively higher strength of the acids was required for the elution than in the batch process.

Use of reaction coil longer than 20 cm produced increased dispersion and reduced the peak height. Hence, a short reaction coil of 20 cm was used. Sharp narrow peaks obtained indicate the faster reaction kinetics of the metal elution. The dispersion for the manifold was calculated by continuously passing 0.5 % potassium permanganate solution through the manifold and by injecting 20 μl of 0.5 % $KMnO_4$ solution through the manifold with microcolumn and without microcolumn (Fig. 5.10). Introduction of the micro column did not influence the obtained dispersion 3.42. Dispersion of the system depends on the volume injected and was observed to be higher for the smaller volumes.

5.13.2.f Calibration plot

The calibration plots for the preconcentration of 5 cm^3 of copper, nickel and zinc solutions of 100 to 500 ng, 40 to 200 ng and 10 to 50 ng concentration respectively were obtained after elution of copper, nickel and zinc with 20 μl of 1.0 M HCl, 2.0 M HCl and 0.5 M HCl respectively. The results were recorded in triplicate (Fig. 5.11). The regression coefficient values were observed to be 0.9946, 0.9941 and 0.9980 for copper, nickel and zinc calibration plots respectively. The absorption can be calculated by using equations :

Absorbance = 0.377 [Cu (II), μg] - 0.0339

Absorbance = 2.212×10^{-3} [Ni (II), μg] - 0.0419

Absorbance = 6.81×10^{-3} [Zn (II), μg] - 0.0246

Fig. 5·10

Dispersion study

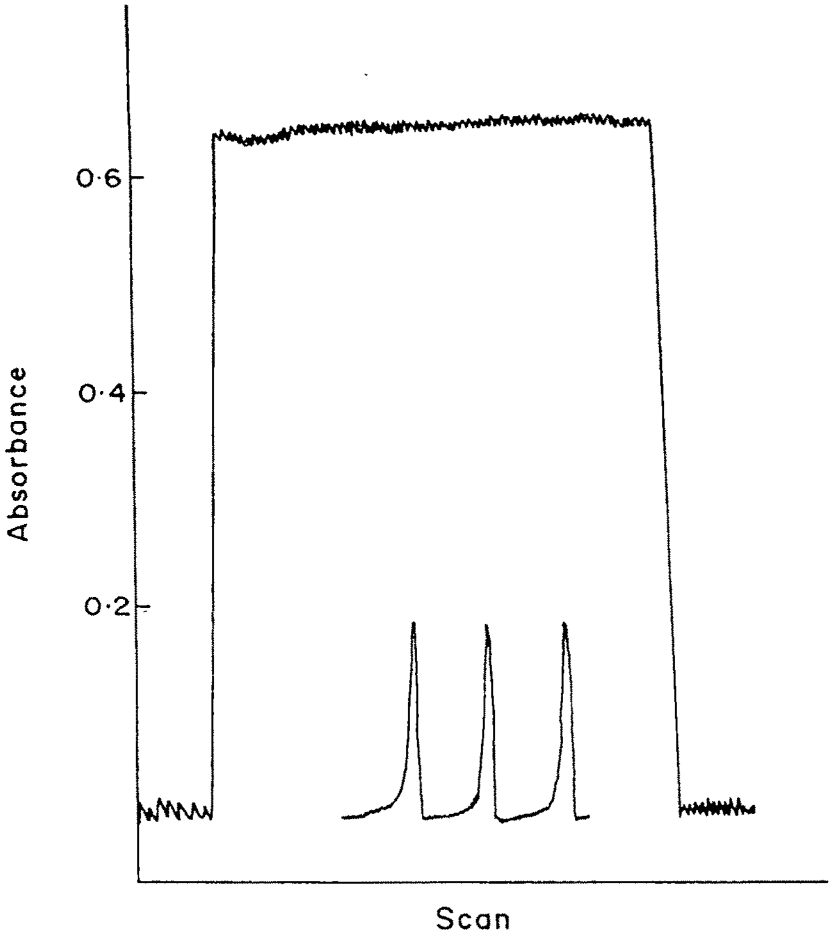


Fig. 5·11

Calibration of copper

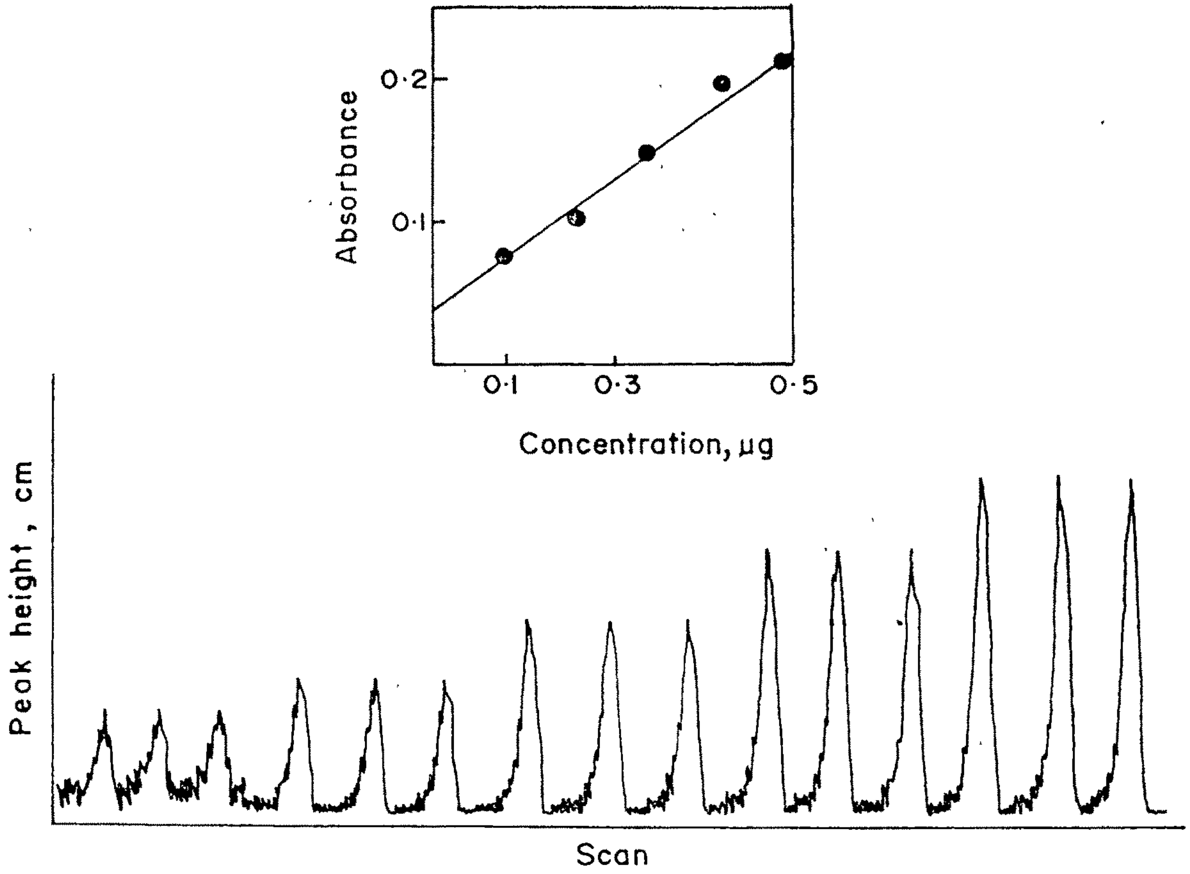
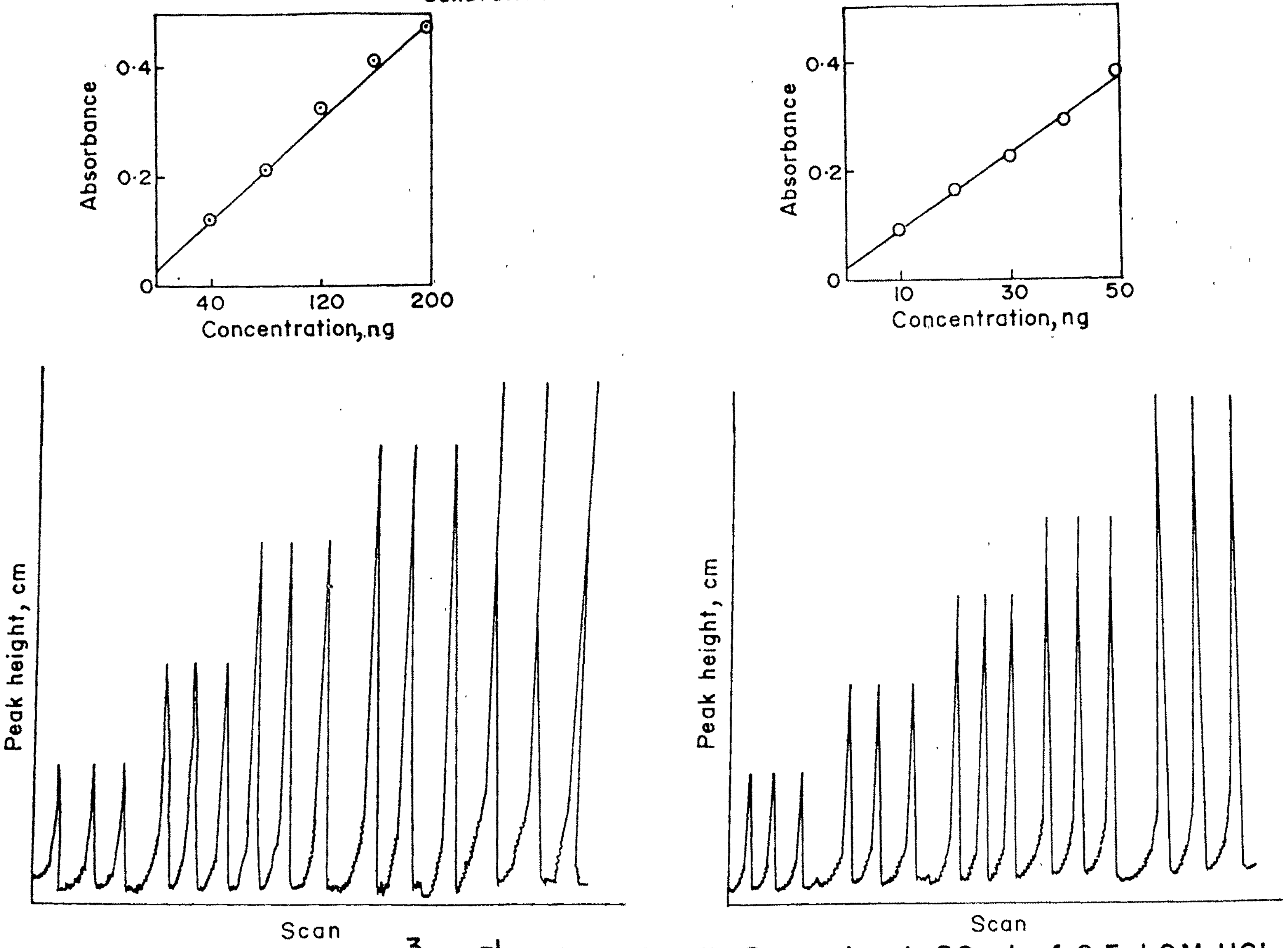


Fig. 5·11

Calibration of Nickle and Zinc



Optimum pH, flow rate 2 cm^3 min^{-1}, column length 2 cm, eluent 20 µl of 0·5-1·0M HCl

●Copper, ⊙Nickle, ○Zinc

respectively for copper, nickel and zinc. The r.s.d. values for copper, nickel and zinc estimation were found to be 3.5 %, 2.14 % and 0.035 % respectively. The lowest detection limit for copper, nickel and zinc was found to be 8, 5 and 0.65 ng cm^{-3} respectively which was based on the three times the standard deviation of the blank signals.

From the study it was observed that the synthesised resin offers effective preconcentration of copper, nickel and zinc at ng levels. It was also observed that sodium diethyl dithio carbamate for copper and nickel and xylenol orange for zinc offers a sensitive method for their estimation in continuous flow method. Continuous recording indicates the quantitative uptake of the metal ions by the resin at optimised conditions.

5.14 Preconcentration of cadmium and mercury

Cadmium and mercury deposition tends to be cumulative in the kidney resulting in the kidney failure and ultimately death. The toxicity of cadmium and mercury is discussed earlier in section 3.5. These metals are estimated by neutron activation, direct coupled FAAS, graphite furnace AAS and X-ray fluorescence. As these methods are complicated and relatively ineffective in simple laboratory, speedy determination of cadmium and mercury after preconcentration has become an essential analytical tool. Flow injection methods can satisfy these requirements. Hence the work done earlier in the online preconcentration of cadmium and mercury in continuous flow methods is discussed here.

5.14.1 Literature survey for the online preconcentration of cadmium and mercury using micro columns

Several methods for the determination of traces of cadmium and mercury have been established. Solvent extraction and chemiluminescence processes for the cadmium estimation were tried by Burguera and Burguera et al[44,45]. Determination of organomercury from biological samples[46,47] and sea water[48,49] was carried out with inductively coupled plasma-mass spectrometry in flow system. However, for online preconcentration of cadmium and mercury in flow system only a few reports are available. Online preconcentration of cadmium complex by solvent extraction was first reported by Kilinghoffer[50] in 1980. Where as the preconcentration of trace mercury with sorbent extraction columns using flow injection techniques was first demonstrated by Ruzicka and Arndal[55] in 1989. In 1984, Malamas et al[22] have tried preconcentration of cadmium on immobilised 8-quinolinol in a microcolumn in f.i.a. system. Leach et al[51] and Lazaro et al[52] used cation exchanger for online preconcentration of cadmium. Fang et al[53,54] have reported online preconcentration method using microcolumns of 8-quinolinol resin for enrichment of Cu (II), Cd (II), Ni (II), Zn (II), Pb (II), Co (II), Ca (II) at ng levels.

In 1989 Tsalev et al[32], Devi et al[56] and in 1991 Micheal et al[58] and Purohit and Devi[36] used online preconcentration methods for cadmium estimation successfully. Oslen et al[21] reported a flow injection method with FAAS for the determination of trace amounts of Cd(II), Pb(II), Zn(II), Cu(II) in polluted sea water using a microcolumn of chelex-100 resin. Online preconcentration method for Cd(II), Hg(II), Pb(II) from sea water in conjuction with inductive coupled plasma mass spectrometry was reported by Wiederin et al[57]. The limit of detection for cadmium and mercury was found to be 0.087 and 0.097 $\mu g\ cm^{-3}$. Online procedures[59,60] have been proposed for mercury preconcentration using columns containing immobilised cysteine, dithiocarbamate or quinolin-8-ol. Garcia et al[61] reported online preconcentration of inorganic and organic mercury using solvent extraction as well as microcolumns filled with diethyl dithiocarbamate, pyrrolidin-1-yldithioformamate and dithizone immobilised on silica C_{18} and cold vapor AAS as detector. The r.s.d. was found to be ± 3.4 % at 0.5 μg/l Hg (II) levels. A brief summery of online methods for these metals is given in Table 5.3 for easy referencing.

The results obtained in the online preconcentration of cadmium and mercury using dithizone anchored poly (vinyl pyridine) resin are discussed here. The experimental details and the manifold used is discussed in section 5.12.2.

5.14.2 Results and discussion

Flow injection manifold used in the present study is illustrated in Fig.5.5 with a uv-visible spectrophotometer as a detecting device. Various components used are described in section 5.7. For the estimation of cadmium and mercury saturated solution of diphenyl carbazide in ethanol and dithizone in DMF was used respectively. Hence in the given manifold channel 1 and 2 were used for the buffer and metal solution respectively. Care of the manifold was taken as mentioned earlier in section 5.13.2.

5.14.2.a Effect of pH on preconcentration of cadmium and mercury

Effect of pH on preconcentration of cadmium and mercury was studied by carrying out the preconcentration of cadmium and mercury by passing metal solutions of pH 1-7 through the column and eluting the chelated cadmium and mercury with 20 μl of 1 M acetic acid and a 1:1 mixture of 0.5 M nitric acid and 2.0 % ammonium

Table 5.3 : Review of literature survey for online preconcentration of cadmium and mercury in flow injection system.

Sr. No.	Ion exchanger or reagent used	Comments	Reference
1	Chelex-100	Determination of Cu(II), Zn(II), Cd(II), and Pb(II) in polluted sea water.	21
2	Immobilised 8-oxine	Cd(II) and Cu(II) at ng level	22
3	Tri-octylamine on silanized glass	Cd(II) at ng level. Eluted with 0.5 M EDTA and 0.3 M HNO_3	32
4	Alumina matrices	Determination of Hg(II)	46,48,49
5	8-Quinolinol resins	Enrichment of Cu(II),Cd(II), Ni(II), Zn(II),Pb(II),Co(II), Ca(II) at ng level	53,54
6	8-Quinolinol-5-sulfonic acid on porous glass	Cu(II),Cd(II),Mg(II),Hg(II), Zn(II) and Pb(II) at ng level	56
7		Determination of Hg(II), Mn(II), Cd(II), Ni(II),Cu(II),Pt(IV),Pb(II) in freeze dried urin	57
8	Chelating resins	Ultratraces of Cd(II),Cu(II), Pb(II) and Ni(II) in water samples	58
9	Chelating resins containing immobilised cystein,dithiocarbamate quinolin-8-ol	Preconcentration of Hg(II)	59,60
10	Diethyl dithio carbamate pyrrolidin-1-yldithioformamate and dithizone immobilised on silica C_{18}	Preconcentration of inorganic Hg(II) and methyl mercury in sea water	61

nitrate respectively. The results are plotted in Fig.5.12 as peak height vs pH. On comparision of the results obtained in the FI system with those from the batch method, it was observed that there is no significant variation in the pH values for the preconcentration of cadmium and mercury by the flow system and by batch method.

5.14.2.b Effect of reagent concentration

In the study of effect of reagent concentration, it was observed that for cadmium, only saturated solution of diphenyl carbazide in ethanol is effective. Where as 0.1 % dithizone solution in DMF is sufficient for mercury. As dithizone being coloured reagent, higher concentration of dithizone gives negative peak. The results are given in Fig.5.13.

5.14.2.c Effect of column length

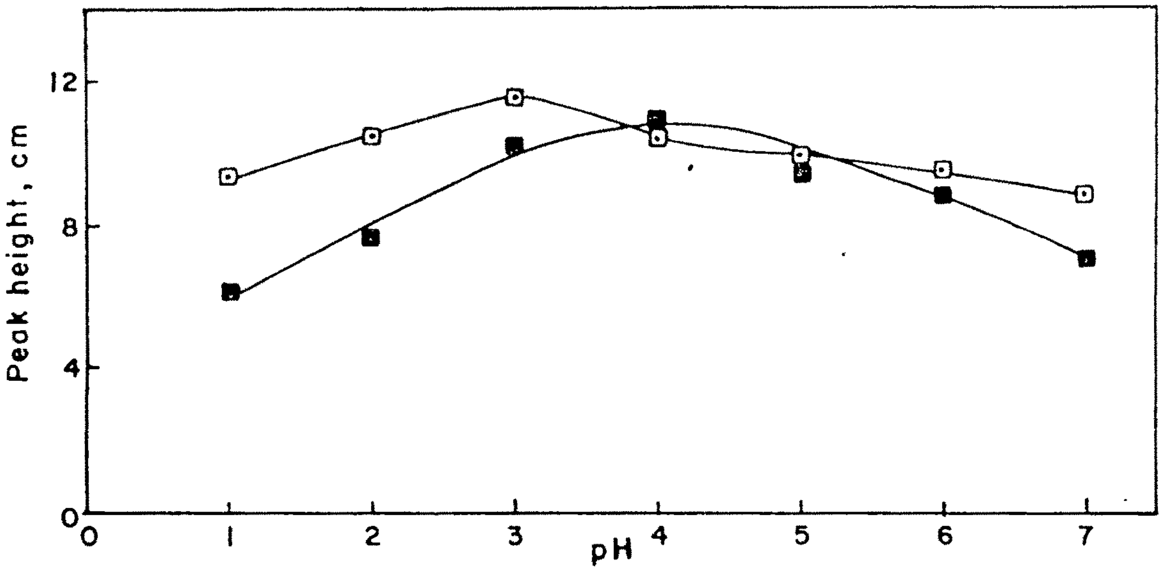
Column length was optimised for cadmium and mercury using 1-4 cm long and 2 mm i.d. glass columns filled with chelating resin as described earlier. From the results obtained, it was observed that 3 cm and 2 cm long columns are effective in preconcentration of cadmium and mercury respectively (Fig. 5.14). Long columns increase the dispersion and hence short column is desirable for the f.i.a. systems.

5.14.2.d Effect of flow rate

Effect of flow rate on preconcentration of cadmium and mercury was studied by varving the flow rate of the solutions in the manifold from 0.5 to 5 cm^3 min^{-1}. It was observed that at lower flow rate broadening of the peaks is considerable where as at higher flow rates a high degree of dispersion is observed resulting into

Fig. 5·12

Effect of pH on preconcentration

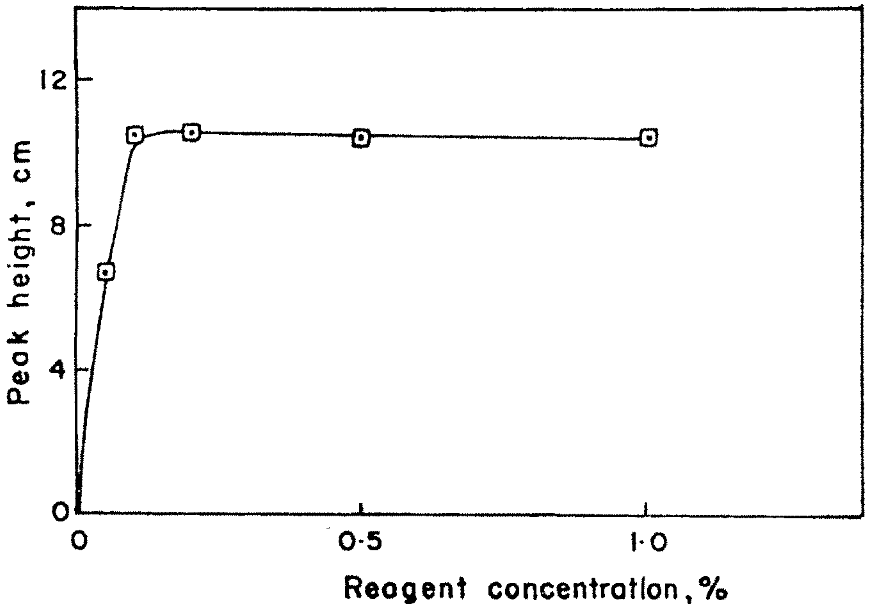


Flow rate 2 cm^3 min^{-1}, metal solution 5 cm^3 of 1 μg cm^{-3}, column length 2 cm, reagent concentration for cadmium saturated solution; for mercury 0·1 % (w/w)

■ Cadmium , ⊡ Mercury

Fig. 5·13

Effect of reagent concentration

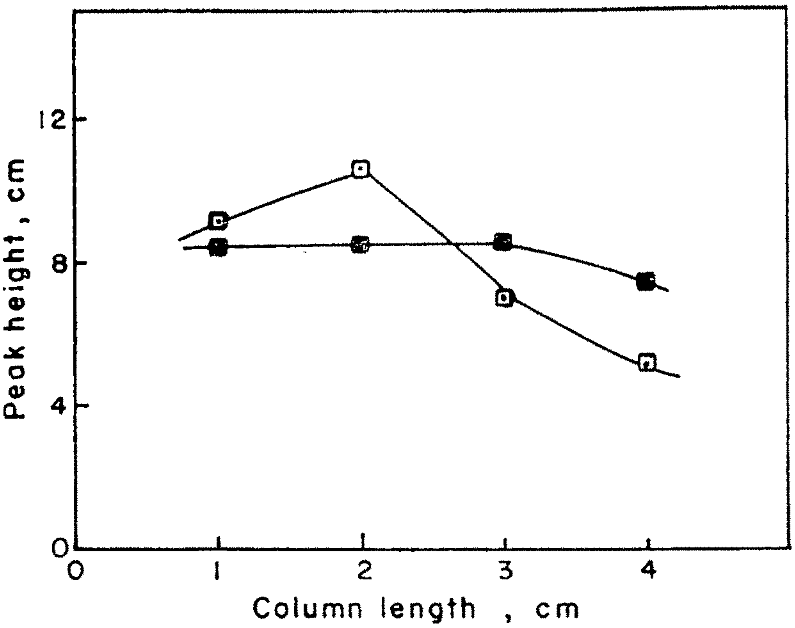


Optimum pH, metal solution 5 cm^3 of 1 μg cm^{-3}, column length 2 cm, flow rate 2 cm^3 min^{-1}, eluent 20 μl of a mixture of 0·5 M HNO_3 + 2·0 % NH_4NO_3

⊡ Mercury

Fig. 5·14

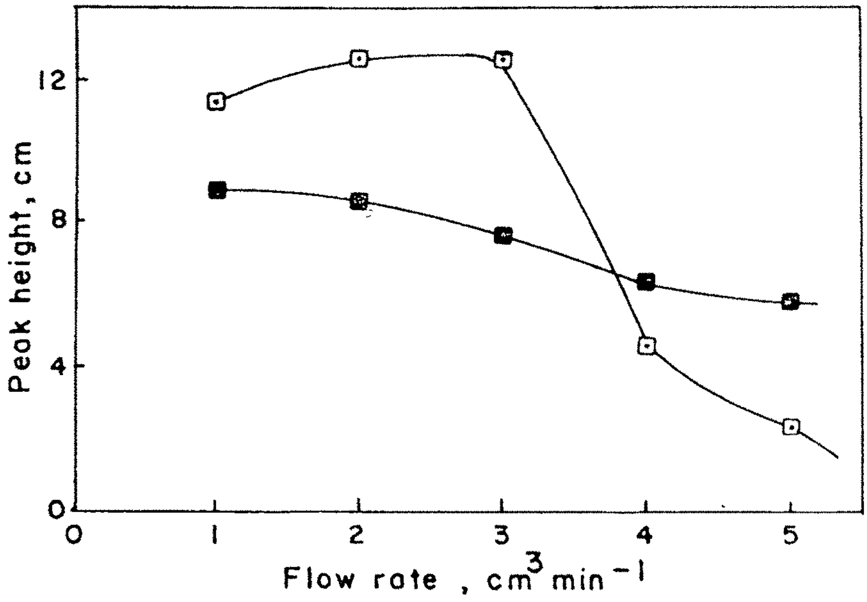
Effect of column length



Flowrate 2 cm^3 min^{-1}, metal solution 5 cm^3 of 1 µg cm^{-3}, optimum pH, eluent 20 µl of 0·5 M CH_3COOH for cadmium and a mixture of 0·5 M HNO_3 + 2·0 % NH_4NO_3 for mercury ■ Cadmium , ⊡ Mercury .

Fig. 5·15

Effect of flowrate



Optimum pH, metal solution 5 cm^3 of 1 µg cm^{-3}, column length 2 cm , eluent 20 µl of 0·5 M CH_3COOH for cadmium and a mixture of 0·5 M HCl + 2·0 % NH_4NO_3 for mercury

■ Cadmium , ⊡ Mercury

reduced peak heights. Results obtained are presented in Fig.5.15. It was found that flow rate of 2 cm^3 min^{-1} is most suitable for quantitative extraction of metal ions by the resin.

5.14.2.e Effect of eluting reagent

Elution of preconcentrated cadmium and mercury from the resin under study was done with 20 µl of HCl, H_2SO_4, HNO_3 and CH_3COOH of 0.1 to 2 M concentrations and with the mixtures of HNO_3 and NH_4NO_3 of various concentrations. % Elution of the metal is given in Table 5.4. It was observed that 2.0 M acetic acid and a 1:1 (v/v) mixture of 0.5 M HNO_3 + 2.0 % NH_4NO_3 quantitatively eluted cadmium and mercury respectively. Continuous elution of cadmium with 2.0 M CH_3COOH and mercury with 0.5 M HNO_3 + 2.0 % NH_4NO_3 mixture gave narrow peaks of comparable heights indicating that the analyte concentration lies in a relatively narrow eluting range.

Use of reaction coil longer than 20 cm produced increased dispersion and reduced the peak height. Hence a short reaction coil of 20 cm was used. The sharp narrow peaks obtained indicate the faster kinetics of elution of the metals. The dispersion was calculated as discussed earlier in section 5.13.2.e and was found to be 3.42 for the manifold used (Fig.5.10). It was also observed that the dispersion of the system depends on the volume injected and was observed to be higher for smaller volumes.

5.14.2.f Calibration plots

The calibration plots for the preconcentration of 5 cm^3 of cadmium solution of 100 to 500 ng and 5 cm^3 of mercury solution of 10 to 50 ng were obtained after elution

Table 5.4 : Study of eluting systems for cadmium and mercury

Optimum pH, flow rate 2 cm^3 min^{-1}, column length 2 cm, metal solution 5 cm^3 of 1 µg cm^{-3}

Sr.	Eluent	% Elution Cadmium	% Elution Mercury
1	M HCl		
	0.1	70.0	00
	0.5	80.0	00
	1.0	83.0	00
	2.0	93.0	00
2	M HNO_3		
	0.1	63.0	23.0
	0.5	69.0	31.0
	1.0	76.0	43.0
	2.0	79.0	50.0
3	M H_2SO_4		
	0.1	66.0	00
	0.5	75.0	00
	1.0	85.0	00
	2.0	86.0	00
4	M CH_3COOH		
	0.1	80.0	00
	0.2	85.0	00
	0.5	99.0	00
	1.0	100.0	00
	2.0	100.0	00
5	M HNO_3 + % NH_4NO_3		
	0.1 + 1.0	13.0	81.0
	0.2 + 1.0	15.0	87.0
	0.5 + 1.0	19.0	92.0
	0.5 + 2.0	19.0	100.0

of cadmium with 20 μl of 2.0 M CH_3COOH and mercury with 20 μl of a 1:1 (v/v) mixture of 0.5 M HNO_3 and 2.0 % NH_4NO_3. Results were recorded in triplicate (Fig.5.16). The regression coefficient values were observed to be 0.9990 and 0.9902 for cadmium and mercury respectively. The absorbance can be calculated by using equations :

$$\text{Absorbance} = 9.33 \times 10^{-3}\,[\text{Cd (II)}, \mu\text{g}] - 0.1477$$

$$\text{Absorbance} = 0.346\,[\text{Hg (II)}, \mu\text{g}] - (-0.0228)$$

respectively for cadmium and mercury. The r.s.d values for cadmium and mercury were found to be 0.24 % and 2.24 % respectively. The lowest detection limit was found to be 17.6 ng cm^{-3} and 2.0 ng cm^{-3} for cadmium and mercury respectively which was based on the three times the standard deviation of the blank signal for the carrier stream.

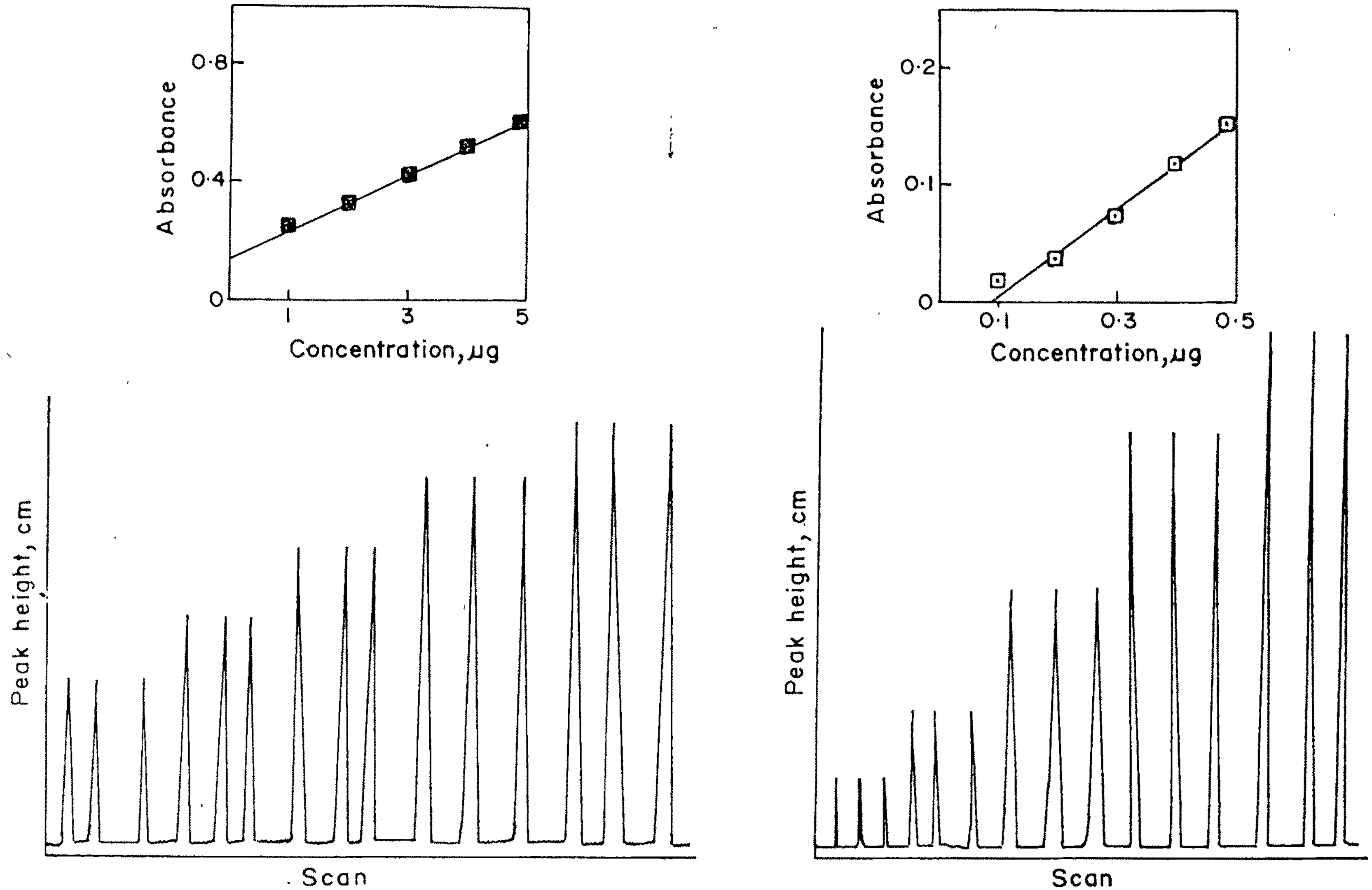
From the study it was observed that the synthesised resin is effective for the preconcentration of cadmium and mercury at ng levels. It was also observed that diphenyl carbazide for cadmium and dithizone for mercury offer a sensitive method for their determination in continuous flow method. Continuous recording indicates the quantitative uptake of the metal ions by the resin at optimised conditions.

5.15 Preconcentration of gold and palladium

With the increasing cost associated with the mining of gold and palladium, it has become necessary to recover ng levels of these metals from the waste samples. Trace amounts of these noble metals are found in mineral, metallurgical, electroplating and environmental samples. The separation and determination of trace amounts of gold and palladium have gained importance due to the limited

Fig. 5·16

Calibration of Cadmium and Mercury



Optimum pH, flow rate 2 $cm^3 min^{-1}$, column length 2 cm, eluent 20 µl of 1M CH_3COOH for Cadmium and 0·5 M HNO_3+2·0% NH_4NO_3 mixture for Mercury

■ Cadmium, ⊡ Mercury

concentration of these metals in nature as well as various types of interferences in both separation and determination. Hence a preconcentration procedure is often needed to increase the concentration levels in the solutions to be analysed and to remove matrix interferences.

5.15.1 Literature survey for online preconcentration of gold and palladium using microcolumns.

Batch and column chromatography are the analytical techniques useful for preconcentration of µg quantities but they have their limitations such as lower exchange rate, tedious process, lower enrichment factor and requirement of large sample volumes. Online column chromatography for preconcentration has improved the detection limit by ten folds and has overcome the problems due to high salt content and interferences. As very limited work is done with these metal ions using flow system, only few reports are available. Betteridge et al[62] have first time developed an online preconcentration method for traces of gold by using FAAS as detecting device. Similar methods[63,64] have been reported for the determination of gold after preconcentration. Falkner and Edmond[65] reported a flow injection method for the determination of gold at femtomolar levels in natural water by inductively coupled plasma-quadrapole mass spectrometry. Taylor[66] and Qi[67] presented methods for the gold analysis with online preconcentration followed by determination using AAS. Taylor et al[66] reported a flow injection method for the determination of traces of gold in cyanide process solution. Preconcentration of the dicyano aurate(I) anion is achieved by extraction into supported liquid membrane on polymeric support. The detection limit was found to be 0.005 mg/l and r.s.d. was 2.7 % at the 0.04 mg/l level.

Gomez and McLeod[68] have reported online separation method for gold from refinary effluent water in flow analysis. They have used Amberlite A-26 and mercaptoacetoxy-cellulose as a support for preconcentration of gold. The detection limit of the method was found to be 1 ng cm^{-3}. Oslen et al[69] developed a method for the determination of palladium by FAAS after preconcentration with flow system. A reverse phase column extraction method has been employed by Davey and Di[70]. Where di(methyl heptyl) methyl phosphonate loaded on to a macroporous resin was used as a stationary phase for online preconcentration of traces of gold. Davey and Di[71] also reported a normal on line column preconcentration in a flow injection method for the separation and preconcentration of noble metals like Pd(II), Pt(IV), Ir(IV) using FAAS detector. Where α-amino pyridine resin was used as a stationary phase. Lin et al[72] developed a method for the determination of palladium after preconcentration using FAAS in flow system. The microcolumns used were packed with activated carbon fibre. The detection limit of the method was 0.3 ng/ml and r.s.d. was 3.9 % at 50 ng/ml. A brief summary of these methods is given in Table 5.5 for easy referencing.

The chelating resin discussed earlier was used in the microcolumn incorporated in a continuous flow system for the preconcentration of gold and palladium. The various experimental conditions were optimised as discussed in section 5.12.2 for achieving desirable preconcentration levels and quantitative elution and estimation of gold and palladium.

5.15.2 Results and discussion

Flow injection manifold used in the present study is illustrated in Fig.5.5. In the given manifold channel 1 and 2 were used for the buffer and metal solution

Table 5.5 : Review of literature survey for online preconcentration of gold and palladium using flow injection system.

Sr. No.	Ion exchanger or reagent used	Comments	Reference
1	Commerical anion exchanger Bio-Rad AG 1 - X 2	Determination of gold at femtomolar level (10^{-15} mol/L) in natural water	65
2	Supported liquid membrane of polysorb MP-1 based on cross-linked styrene-DVB	Preconcentration of Au(III)	66
3	Natural phosphine oxide as a functional group linked to an inert fibre 8531.	Preconcentration and separation of gold from ores and metallurgical samples	67
4	Amberlite A-26 and mercaptoacetoxy-cellulose as a support	Separation of Au(III) from refinary effluent water	68
5	Activated carbon fibre	Determination of Pd(II) after preconcentration	69,72
6	Di(methyl heptyl) methyl phosphonate loaded on to a macro-	Preconcentration and determination of traces of Au(III) porous resin	70
7	α -amino pyridine resin as an immobilised support	Preconcentration and separation of Pd(II),Pt(IV),Ir(IV)	71

respectively and channel 3 for the reagents sodium diethyl dithiocarbamate and dithizone respectively for gold and palladium estimation. Care was taken during operation of manifold to avoid mixing of solutions and deposition of reagents on the walls of the tubing. Periodic cleaning of the system was done and the system was purged with water thoroughly before closing for the day.

5.15.2.a Effect of pH on preconcentration of gold and palladium

Preconcentration of gold and palladium was carried out at pH 1-7. The results obtained in this study are given in Fig.5.17 in the form of peak height vs pH. Gold and palladium from the column were eluted by injecting 20 μl of a mixture of 0.2-0.5 M HCl and 2.0 % thiourea. It was observed that there is no effect of pH on the exchange of gold and palladium with the resin. The results obtained in flow system and in batch method show similar trend. In both the methods metal exchange was observed to be pH independent.

5.15.2.b Effect of reagent concentration

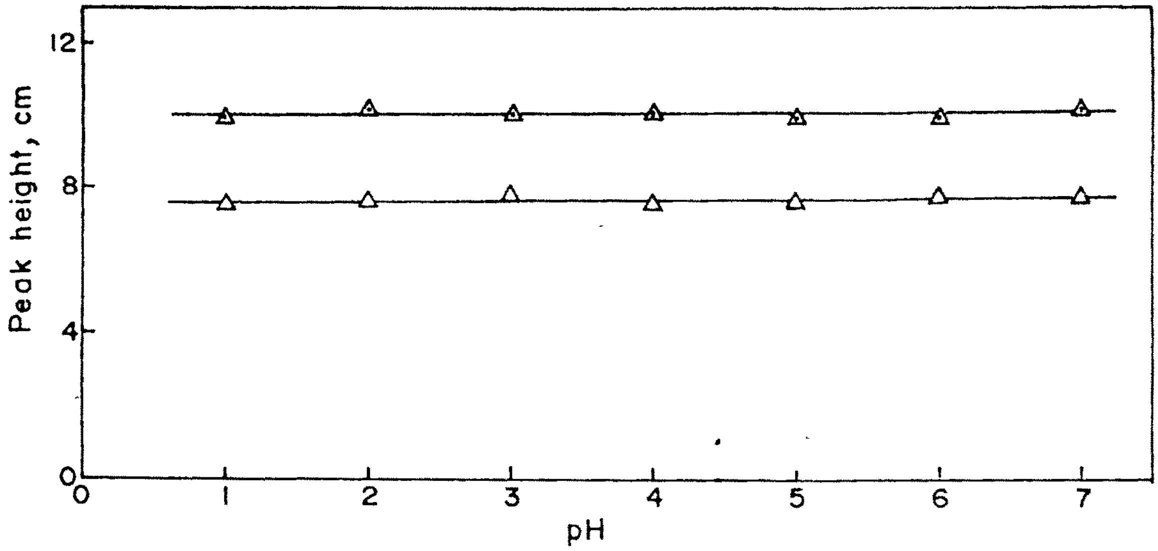
In the study of effect of reagent concentrations (varying from 0.2-2.0%), it was observed that 0.2 % aqueous solution of sodium diethyl dithiocarbame for gold estimation is sufficient. Where as for palladium, 0.1 % dithizone in DMF is sufficient. The results are given in Fig. 5.18.

5.15.2.c Effect of column length

Column length was optimised for each metal under study using 1-4 cm long and 2 mm i.d. glass columns. Columns filled with the resinuous material were prepared as described earlier. A 2 cm long column was sufficient for effective

Fig. 5·17

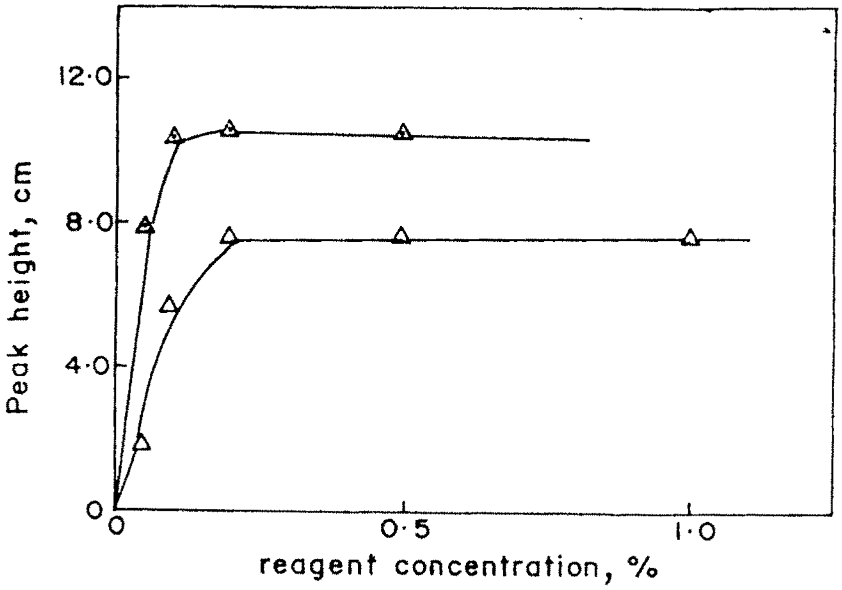
Effect of pH on preconcentration



Flow rate 2 cm^3 min^{-1}, metal solution 5 cm^3 of 1 µg cm^{-3}, column length 2 cm, reagent concentration 0·1 − 0·2 % (W/W)

Fig. 5·18

Effect of reagent concentration



pH − 5, metal solution 5 cm^3 of 1 µg cm^{-3}, column length 2 cm, flow rate 2 cm^3 min^{-1}, eluent 20 µl of 0·2 − 0·5 M HCl + 2·0 % thiourea mixture

△ Gold, ◬ Palladium

preconcentration of gold and palladium. The results in terms of peak height vs column length are given in Fig. 5.19. A 2.0 cm long column was used throughout the study.

5.15.2.d Effect of flow rate

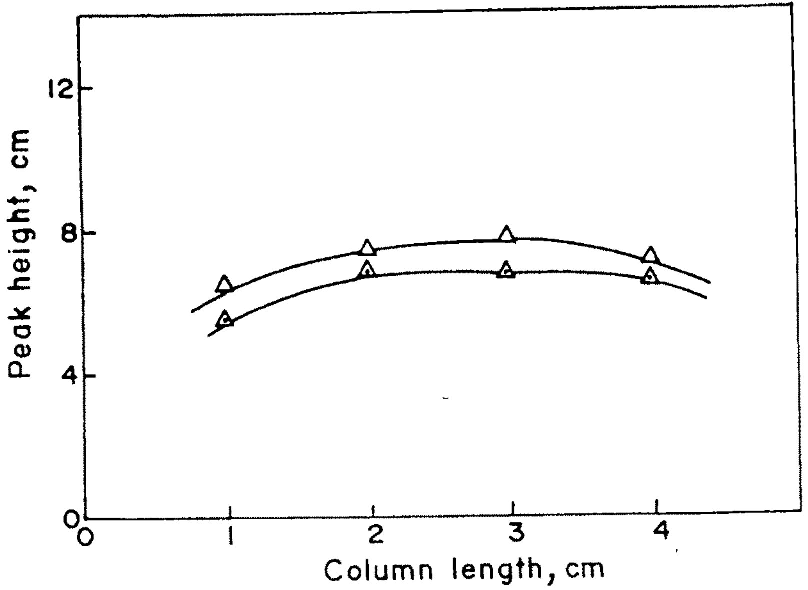
Effect of flow rate on preconcentration of gold and palladium was studied by varying the flow rates in the manifold from 0.5 to 5 cm^3 min^{-1}. It was observed that at lower flow rate (i.e. < 1cm^3 min^{-1}) broadening of the peak is considerable where as at higher flow rate (i.e. > 3 cm^3 min^{-1}) high degree of dispersion is observed resulting into reduced peak heights. Results obtained are presented in Fig. 5.20. Flow rate upto 2 cm^3 min^{-1} and 3 cm^3 min^{-1} was observed to be desirable for gold and palladium respectively and 2 cm^3 min^{-1} flow rate was used throughout the study.

5.15.2.e Effect of eluting reagent

Elution of preconcentrated metal from the resin under study was done with 20 µl of 1.0 to 2.0 M HCl, H_2SO_4, HNO_3, CH_3COOH, a mixture of 0.1 - 0.5 M HCl and 2.0 % thiourea and a 1:1 mixture of 5.0 M HCl and 1.0 M HNO_3. % Elution of the metal is given in Table 5.6. It was observed that only acid could not elute gold and palladium. However, a mixture of 0.2 - 0.5 M HCl and 2.0 % thiourea could elute gold and palladium quantitatively. A 1:1 mixture of 5.0 M HCl and 1.0 M HNO_3 could elute gold partly. Continuous elution of gold using 0.5 M HCl + 2.0 % thiourea mixture and palladium with 0.2 M HCl + 2.0 % thiourea mixture gave narrow peaks of comparable heights indicating that the analyte concentration lies in a relatively narrow eluting range.

Fig. 5·19

Effect of column length

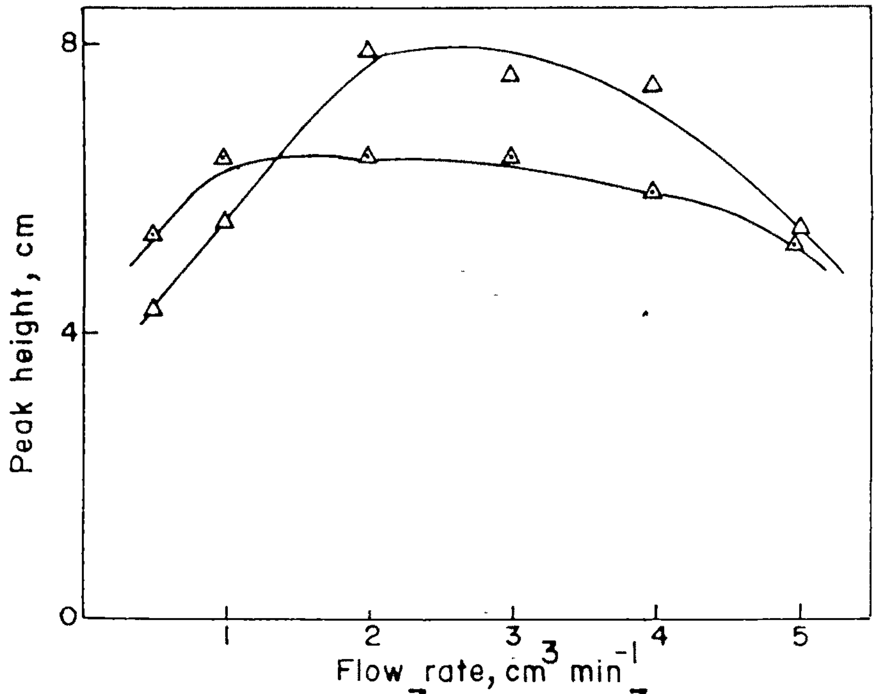


Flow rate 2 cm^3 min^{-1}, metal solution 5 cm^3 of 1 μg cm^{-3}, pH−5, eluent 20 μl of 0·2−0·5 M HCl + 2·0 % thiourea mixture

△ Gold, ▲ Palladium

Fig. 5·20

Effect of flow rate



pH−5, metal solution 5 cm^3 of 1 μg cm^{-3}, column length 2 cm, eluent 20 μl of 0·2−0·5 M HCl + 2·0 % thiourea mixture

△ Gold, ▲ Palladium

Table 5.6 : Study of eluting systems for gold and palladium

pH 5, flow rate 2 cm^3 min^{-1}, column length 2 cm, metla solution 5 cm^3 of 1 μg cm^{-3}.

Sr No.	Eluent	% Elution Gold	Palladium
1.	M HCl		
	0.1	00	00
	0.5	00	00
	1.0	00	00
	2.0	00	00
2.	M HNO_3		
	0.1	00	00
	0.5	00	00
	1.0	00	00
	2.0	00	00
3.	M H_2SO_4		
	0.1	00	00
	0.5	00	00
	1.0	00	00
	2.0	00	00
4.	M CH_3COOH		
	0.1	00	00
	0.5	00	00
	1.0	00	00
	2.0	00	00
5	M HCl + % thiourea		
	0.1 + 2.0	97.0	93.0
	0.2 + 2.0	100.0	100.0
	0.5 + 2.0	96.0	100.0
6	M HCl + M HNO_3		
	1 + 1	00	00
	2 + 1	13.0	00
	3 + 1	53.0	00
	5 + 1	94.0	00
7	% Thiourea		
	1.0	80.0	86.0
	2.0	80.0	85.0
	3.0	80.0	86.0

Use of reaction coil longer than 20 cm produced increased dispersion and reduced the peak height. Hence, a short reaction coil of 20 cm was used. The sharp narrow peaks obtained indicate the faster reaction kinetics with the metals. The dispersion for the manifold was determined as discussed earlier in section 5.13.2.e and was observed to be 3.42 (Fig. 5.10). Dispersion of the system was observed to depend on the volume injected and was observed to be higher for smaller volumes.

5.15.2.f Calibration plots

The calibration plots for preconcentration of 5 cm^3 of gold solution containing 200 to 1000 ng gold and 5 cm^3 of palladium solution containing 1000 to 5000 ng of palladium was obtained after elution of gold and palladium with 20 µl of 0.5 M HCl + 2.0 % thiourea and 0.2 M HCl + 2.0% thiourea mixture respectively. Results are recorded in triplicate (Fig. 5.21). The regression coefficient values were observed to be 0.9853 and 0.9807 for gold and palladium respectively. The absorbance can be calculated by using equations

$$\text{Absorbance} = 0.0645\,[\text{Au(III)}, \mu g] - 0.0841$$

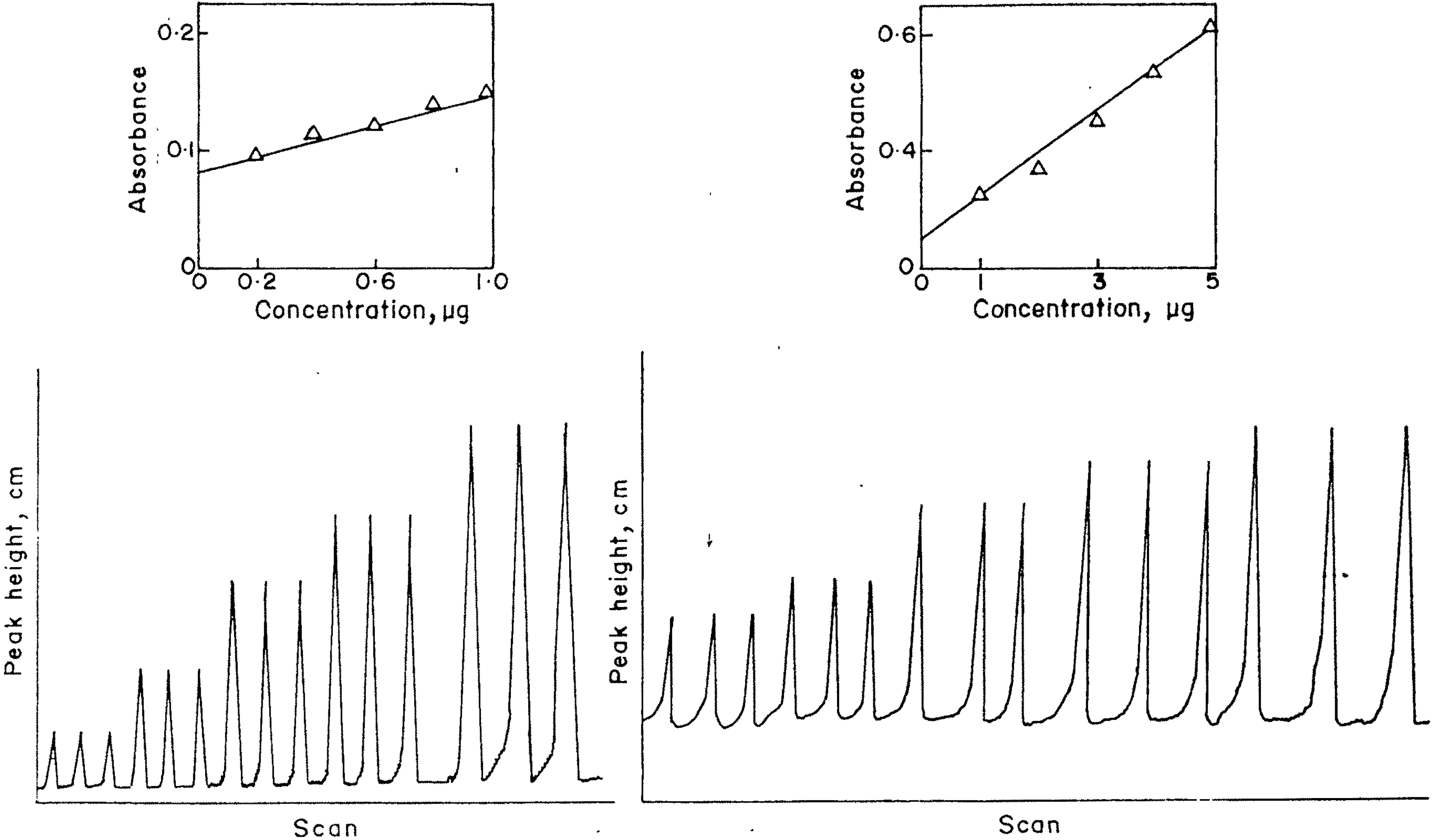
$$\text{Absorbance} = 0.1043\,[\text{Pd(II)}, \mu g] - 0.1429$$

respectively for gold and palladium. The r.s.d. values for gold and palladium were found to be 0.73 % and 1.26 % respectively. The lowest detection limit for gold and palladium was found to be 5.6 and 93 ng cm^{-3} respectively.

From the study it was observed that the synthesized resin offers effective preconcentration of gold and palladium at trace levels. It was also observed that sodium diethyl dithiocarbamate for gold and dithizone for palladium offer a

Fig.5·21

Calibration of Gold and Palladium



pH-5, flow rate 2 cm^3 min^{-1}, column length 2 cm, eluent 20 µl of 0·2–0·5 M HCl +2% thiourea mixture

△ Gold, ▲Palladium

sensitive method of determination in continuous flow method. Continuous recording indicates the quantitative uptake of the metal ions by the resin at optimised conditions.

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