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Flow system for liquid–solid extraction and pre-concentration using a renewable extracting solid phase

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Abstract

A mechanised flow system is described aimed at extracting and pre-concentrating metal ions in a renewable water-insoluble solid phase containing a suitable ligand. The main difference between the proposed system and previously described ones for use with liquid–solid extraction is in the renewable characteristics of the solid phase, which allows for refreshing the extracting surface to be employed between pre-concentration operations. The renewable feature imposes no demands in terms of reversibility of the adsorption process as all the solid organic phase containing the complexed metal is dissolved by a non-aqueous solvent and carried to the detection system. Simultaneously, the system promotes a better compromise between metal extraction and pre-concentration as lower solvent volumes can be used to recover the absorbed species. The system has been evaluated for Zn(II) extraction in order to optimise its main geometrical and chemical variables. A simple spectrophotometric detection system employing a light emitting diode (LED) and a silicon photodiode was employed in these studies. Concentration gains of 42 and detection limits below 1.0 $\mu g\,l^{-1}$ were obtained. Sample throughput and sample consume depend on the desired pre-concentration. For higher (>40) concentration factors, about 40 ml of aqueous sample and a total processing time of 20 min per sample are required.

Keywords: Renewable; Photodiode; Spectrophotometric

1. Introduction

Recently, efforts to improve the sensitivity of analytical methodologies have promoted an intensive search for in-line pre-concentration procedures in flow systems. Liquid–liquid extraction has been investigated [1–4] but the pre-concentration gain is restricted by the difficulty of working in flow systems with higher aqueous/organic volume ratios. Repetitive extraction, using the same organic phase volume, and optimised organic phase composition can help to improve the pre-concentration characteristics of the liquid–liquid extraction flow systems [5,6].

Liquid–solid extraction has been common place in flow systems since the pioneering works employing ion exchange resins [7,8] through the more recent contributions which describe the use of reactive solid phases and “in situ” monitoring of the absorbed species [9–12]. The main drawbacks of the latter procedures are in the lack of reversibility and stability of the reagent in the solid phase. Flow injection analysis has been the preferable flow technique employed to mechanise the liquid–solid extraction because, in most

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cases, the solid phase is retained in a small column inserted on the way to the detector. The literature reports on pre-concentration gains >40 in many cases. However, the inherent dispersion caused during analyte elution from the solid phase in a non-segmented flow system reduces the gain for pre-concentration. The use of an air segmented flow system is not indicated with column based flow manifolds because the passage of air bubbles and their trapping inside the column will deteriorate the precision of the measurements.

The use of liquid–solid extraction batch procedures where the entire extracting solid phase is, after pre-concentration, dissolved in a suitable solvent (usually an organic one) in order to recover the absorbed analyte for detection, is also employed. In this process, the solid phase is prepared to contain a suitable ligand which reacts with the analyte and simultaneously retains the complex in the solid matrix. The whole solid phase is dissolved in an organic solvent, and transferred to a volumetric flask, diluted and presented to various detection techniques [13–15]. Obviously, this procedure employs a new organic phase for each extraction and reversibility of the absorption process is not required. On the other hand, this aspect imposes some difficulties for the mechanisation of the procedure by, for example, a flow analysis approach. In fact, no flow system has been described thus far aimed at employing this concept of liquid–solid extraction. Here, the apparent difficulty is in renew the solid phase between successive extractions.

The solid matrix containing the ligand can be an organic solid such naphthalene or any other compound from which the ligand presents good solubility and that can be dissolved in an organic solvent in order to recovery the analyte. The batch procedure aims at 100% absorption and recovery. The concentration gain is obtained by the ratio between the volume of the aqueous phase from which the analyte is absorbed and the volume of the organic phase employed to dissolve the solid phase after extraction. Typical gains are in the range of 20–100.

In this paper, a new flow analysis approach is presented to mechanise the liquid–solid extraction procedure with recovery of the organic phase after dissolution and spectrophotometric detection of the extracted analyte. The development and evaluation of the characteristics of the system has been made by employing Zn(II) as analyte and 1-(2-pyridylazo)-2-naphthol (PAN) incorporated in naphthalene as the extracting solid phase.

2. Experimental

2.1. Reagents and solutions

All reagents were of analytical grade. Distilled/deionised water was employed throughout. The extracting reagent solution containing PAN and naphthalene were prepared by dissolving a given mass of these solid compounds in an suitable volume of pure absolute ethanol. Zinc(II) standard stock solutions and all the other metal ion solutions (Ni(II), Cu(II), Cd(II), Al(III), and Pb(II)) were prepared from their nitrate salts to contain 1.00 mg l^{-1} of the metal ion. The solutions were 1.0×10^{-3} mol l^{-1} of HNO_3. The final standard solution presented to the extracting flow system were obtained by suitable dilution and their pH were maintained at 7.0 using a carbonate/bicarbonate buffer.

2.2. Flow system and extraction procedure

Fig. 1 shows the schematic diagram of the flow system proposed to mechanise the liquid–solid extraction procedure based on final dissolution of the solid phase and its renewal before each extraction/pre-concentration process. Fluids are impelled using a peristaltic pump (Ismatec MP-13) supplied with Tygon tubing for aqueous and Viton tubing for ethanolic solutions, of variable diameters as required to attain the desired flow rate for each solution. A microcomputer and a home made interface described elsewhere [16] were employed to control the system. The interface contains the digital input/output lines and a 10 bit resolution analogue-to-digital converter employed for control and data acquisition, respectively.

The system consists of five way PTFE piece to which five PTFE three-way solenoid micro-valves (NR-225TO31) were connected. In the upper part of the PTFE piece, an extraction tube was connected and maintained in the vertical position. The off state of the valves causes the respective streams to be returned or deviated from the extraction tube. An additional three-way valve was connected at the end

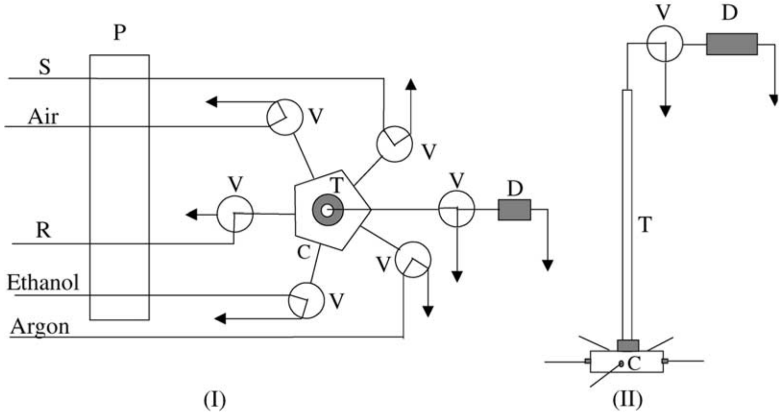

Fig. 1. Flow system for liquid–solid extraction with renewable solid phase. Part (I): overall view of the flow system—S, sample; R, reagent solution containing the solid support and the ligand; V, three way solenoid valves; C, five way connector; T, extraction tube; D, detector. Part (II): side view of the extraction system.

of the extraction tube and used to isolate the detector unit during the extraction steps.

The detection unit was assembled by using a green light emitting diode (LED) ($\lambda_{max} = 560$ nm) and a photodiode with an internal pre-amplifier (RS 308-890). The flow cell was simply a glass tube with 2 mm i.d., moulded in a "U" format and covered with a black PTFE block. The volume of the flow cell and its optical path were estimated as 100 μl and 1.5 cm, respectively. The LED was kept off until a spectrophotometric measurement was requested. The dark current was measured just before the sample solution reaches the detector. The LED was turned on and the intensity data were acquired during the liquid segment passage through the flow cell. A reference signal obtained with a segment of absolute ethanol was employed to calculate the transmitance of the sample solution.

The volumes of the different solutions were admitted to the extraction tube by controlling the time interval the respective valve was kept on. To improve the precision of the admitted volume an optical reflective device, similar to that previously described [17], was adapted to the roller of the peristaltic pump in order to synchronise the valve action with the position of the roller. In this way the effect of flow pulsation on the delivery of small volumes is minimised.

A program written in Visual Basic 4.0 was developed and employed to control the flow system and for data acquisition from the detection unit. The signals were stored and graphically shown, along with their numerically expressed height, in real-time on the screen of the computer monitor.

The sequence of steps necessary to perform a total extraction/determination cycle are:

1. The valves of air and ethanol streams are opened simultaneously and a segmented washing flow is maintained for the washing time, t_w.
2. The air stream switching valve is turned off and a segment of 200 μl of ethanol is admitted and carried by the air stream to the flow cell where the reference signal (100% transmitance) is measured. The segment is discharged and the valve is turned off.
3. The argon valve is opened and enough time (t_d, drying time) is allowed for the extraction tube to dry.
4. The two valves of the reagent (containing a ethanolic solution of naphthalene and PAN) and carrier air are simultaneously opened for t_a, time of reagent adsorption, and a reproducible volume of the segmented reagent is admitted to form a liquid layer all long the inner tube wall. After reagent admission, the respective valve is closed and the air stream carries the segmented reagent.
5. The air stream valve is turned off and the argon stream valve is switched on during the reagent

drying time, t_{rd}, in order to dry the liquid layer, forming a solid naphthalene layer containing PAN on the tube wall.

6. The argon stream valve is switched off and the air and sample valves are turned on. An air segmented stream of sample is passed through the tube. The flow is maintained for t_{pc}, the pre-concentration time. The value of this time interval is determined by the degree of pre-concentration selected by the user.
7. The sample and air streams are stopped. The argon stream is passed for a time interval equivalent to $5 \times t_d$ in order to dry the aqueous layer remaining after the sample passage as much as possible.
8. A volume of absolute ethanol equal to that of the reagent mixture is passed through the tube carried by the air stream. It must be remembered that this volume should be only enough to cover the solid organic layer present in the tube wall.
9. The air stream is momentary stopped and a extracting volume of ethanol is admitted. The air stream is re-activated and carries the ethanol segment which dissolves and removes the solid phase containing the extracted/pre-concentrated analyte. The plug is passed through the detector with the preceding valve kept on. The intensity is measured and the absorbance is accessed.
10. Step number 1 is repeated and the system is cleaned and stands ready for another extraction/pre-concentration cycle starting from step 3, because a new reference signal (100% transmitance) is not necessary for successive extractions.

All 10 steps are automatically effected after the user has supplied the controlling program with the required time intervals.

3. Results and discussion

3.1. Preliminary studies

The preliminary experiments were carried out to observe the overall behaviour of the flow system and of the liquid–solid extraction approach. Initially an extraction tube (T) made of glass (40 cm long and 2.0 mm i.d.) was employed. Concentrations of PAN and naphthalene (30–1000 mg, respectively) were maintained in the same proportion as recommended by the manual procedure for Zn(II) analysis [18]. The precision of the detection system and a preliminary analytical curve obtained for concentration of Zn(II) in the range 10–200 $\mu g\, l^{-1}$ was obtained. The precision obtained for a pre-prepared complex of PAN with 2 ppm of Zn(II) was 0.003 A, for an average signal of 0.306 A. This precision is considered adequate for the purpose of this work. During the initial experiments it was also observed that the precision of the entire process for a solid phase containing a pre-formed Zn(II)/PAN complex, its deposition and its re-dissolution was not good, with a standard deviation about 10 times greater than the values found for the Zn(II)/PAN complex in alcoholic solution.

The analytical curve showed the expected saturation of the signal for Zn(II) concentrations above 100 $\mu g\, l^{-1}$. The signals were obtained by pumping 9.0 ml of the aqueous buffered solution of the metal in a segmented way at 60 $\mu l\, s^{-1}$, as described above. The linear range extended from 10 to 100 $\mu g\, l^{-1}$.

However, during the experiments it was observed that the convection movement caused by the segmented flow removes the solid phase from the glass tube wall. This fact deteriorates the repeatability of the process. New experiments were performed pumping the sample without segmentation. Reproducible results were obtained because, in the absence of the turbulent flow, the solid phase is retained on the glass surface. However, the sensitivity was reduced largely because of non-effective mass transport. An useful linear analytical curve was obtained for the range 50–350 $\mu g\, l^{-1}$.

Attempts were made in order to replace the solid support of the complexing agent. Paraffin, stearic acid and β-napthol were evaluated with no promising results. None of these alternatives resulted in an improvement relative to fixation of the solid extracting phase on the glass wall.

Some experiments were made by using metallic tubes of same dimensions as the glass tube. Many retained the solid phase. However, contamination was a serious problem, for example, in a stainless steel tube. On the other hand, a preliminary experiment with aluminium foil demonstrated that the solid naphthalene containing PAN adheres strongly to the surface and no colour change was observed either in the adhered solid phase or in the ethanolic solution, after re-dissolution.

This fact indicates that an aluminium surface promotes no significant metal/PAN complex formation.

After these preliminary investigations, an aluminium tube 32 cm long with 2.0 mm i.d. was employed for the optimisation of the flow system. The tube material was identified as an alloy (6063) and has been analysed. Its composition in wt.% was found to be Al-99.56%, Cu-0.028%, Zn-0.028%, Fe-0.110%, Mg-0.260% and Mn-0.013%. The tube was used after its inner surface has been treated with a 10% hydrochloric acid solution.

3.2. *Performance of the extracting system*

The aluminium tube was found to retain the naphthalene containing PAN and it was possible to work with segmented flow in order to improve mass transport to the absorbing surface. The ratio between the PAN and naphthalene was chosen considering that the system is being developed to work with low (below 10 μg l^{-1}) metal concentrations. The compromise is, therefore, with the value of the blank which, in view of the PAN absorbance at the detection wavelength, should be kept as low as possible. The reagent solution concentration was selected as 6 mg of PAN and 1000 mg of naphthalene in 50.0 ml of ethanol. This solution will undergo a four times dilution during the extraction process (because the volume of ethanol employed for dissolution of the solid layer, 200 μl, is four times greater than the volume of the ethanolic PAN/naphthalene solution used to form the layer, 50 μl) and will then present an absorbance value of about 0.020.

The effective gain in the concentration of Zn(II) was estimated as 42 times, since a 12 μg l^{-1} Zn(II) solution produced an absorbance equivalent to a 503 μg l^{-1} under the conditions described in Table 1. This gain has the same magnitude as found by the optimised conventional batch procedure. However, the overall mass recovery is only about 20%.

The detection limit under the conditions established in Table 1 was found to be 0.8 μg l^{-1} after determination of the standard deviation of the blank. The analytical curve is linear in the range from 1 to 12 μg l^{-1} ($r = 0.9984$). For Zn(II) concentrations above 12 μg l^{-1} the analytical curve approaches a plateau which allows the determination to be processed only for Zn(II) concentration below 30 μg l^{-1}. Extension of the useful analytical range can be obtained by reducing the sample delivered volume, at the cost of sensitivity and detection limit.

Table 1
Typical parameters values employed for Zn(II) pre-concentration in the liquid–solid extraction flow system

Parameter	Value
PAN/naphthalene extraction solution	6 mg/1000 mg in 50.0 ml of ethanol
Washing time interval (s) (volume, ml)	25 (1.5)
Total drying time interval[a] (s)	490
Volume of extracting solution (μl)	50
Volume of extracting ethanol (μl)	200
Sample volume (ml) (delivery time, min)	45.0 (12)
Argon flow rate (ml min^{-1})	300

[a] Time taken, 70 s for drying the solid phase, 350 s for drying the sample residue and 70 s after the cleaning procedure.

The main restricting factor of the present methodology is in the time necessary to obtain a large pre-concentration gain (ca. 20 min per sample, for a 42 times gain in concentration). The main restricting time intervals are the sampling time interval and the sample drying time interval (720 s are necessary to pump 45 ml of sample and 350 s are employed for drying the liquid film before re-dissolution with the ethanol plug). Obviously, the sampling time can be reduced at the cost of sensitivity by reducing the sample volume or increasing its flow rate. Neither is satisfactory if sensitivity is the main concern. The system has not been optimised to reduce the drying time interval. This could be done by using, for example, a pre-heated gas flow. Additionally, it should be emphasised that the requirement for the drying time interval arises because spectrophotometric detection has been employed. Homogenisation of an organic/aqueous film is difficult and more reproducible results, with the simple spectrophotometric detection system employed in this work, are obtained if the solid film is dissolved in ethanol in the absence of water. However, if another detection technique, such as flame atomic absorption or graphite furnace electrothermal atomisation is employed, the last drying time would not be necessary. Obviously, in addition, the use of such detection techniques would impart the advantage of improvement on the selectivity of the method. One attractive solution to reduce the time interval necessary for the analysis should be to construct a parallel

Table 2
Comparative absorbance signals for 8.0 μg l^{-1} of the metal ion analysed in the proposed system under the conditions specified in Table 1

Analyte	Absorbance
Zn(II)	0.057
Cd(II)	0.041
Cu(II)	0.112
Ni(II)	0.137
Al(III)	0.074
Pb(II)	0.061

manifold with two or more columns which could, in principle, divide the total analysis time by the number of columns present in the system.

In the present form, the overall precision obtained, expressed as the absolute standard deviation, for 10 absorbance signals of a solution containing 12 μg l^{-1}of Zn(II) and for the blank, is 0.025. In this system a complete cycle is performed in about 20 min per sample, with a 42 times gain in the concentration.

The complexing agent employed in this work (PAN) is not selective at the pH at which samples have been conditioned. Table 2 shows comparative signals for other selected metal ions. It can be concluded that the methodology employing PAN as complexing agent is not suitable for the determination of metal ions without a prior separation procedure. On the other hand, the method could be employed for screening water samples for the presence of heavy metals to direct the samples with absorbances higher than a pre-established threshold to a complete chemical analysis [19]. Furthermore, the method could be employed for water analysis with the aid of more selective extracting reagent, screening of wastewater with perhaps reduced sample volume as the concentration of elements in such samples may be greater than for surface and drinking water.

4. Conclusion

This work proposes a new flow analysis method to perform liquid–solid extraction and pre-concentration using renewable solid phase extraction. The approach has demonstrated a good sensitivity and can be used for screening samples with a very simple and inexpensive spectrophotometric detection system.

In the present study, a non-selective complexing agent (PAN) has been employed and, therefore, a non-selective response to metal ions was obtained. However, the proposed methodology opens a fertile field to be exploited regarding the extraction and pre-concentration of analytes in flow analysis.

As immediate advantages over the batch procedure, one could mention the low reagent and sample consumption with the same concentration gain and the automatic processing of the sample with all steps being controlled and effected under computer control.

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