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RECOMMENDATIONS FOR
PUBLICATION OF PAPERS ON A
NEW ANALYTICAL METHOD BASED
ON ION EXCHANGE OR ION-
EXCHANGE CHROMATOGRAPHY

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RECOMMENDATIONS FOR PUBLICATION OF PAPERS ON A NEW ANALYTICAL METHOD BASED ON ION EXCHANGE OR ION EXCHANGE CHROMATOGRAPHY

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Abstract - The operations with ion exchangers used in analytical chemical procedures are classified into three groups: simple ion exchange operations, ion exchange chromatography and ion exchangers used as carriers. All the important points, which have to be considered for the preparation of a paper dealing with ion exchangers are given for all three groups. The points include specifications, pretreatment and regeneration of the ion exchanger used and all those, which give complete information and verification of the efficiency and confidency of an analytical method.

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INTRODUCTION

Ion exchangers (resins or other solid materials suitable for ion exchange) are widely used in analytical laboratories as a preliminary chemical operation for the enrichment of trace amount of metals, other ions or ionic and non ionic organic substances, for separation of interfering ions or elements or simply to change the ionic composition of an electrolyte, or to convert a salt to acid or vice versa.

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Valuable comments from N.M. Rice (UK) are also appreciated.

Beside the use of ion exchangers for the above operations or purposes, there is another wide application field of ion exchangers: ion exchange chromatography.

Although in some cases it is difficult to distinguish between the two fields of application the following statements can be made:

In the first field of applications (enrichment, separation of interfering substances, impurities, salt splitting, change of composition of a solution, etc.) the exchange of certain ions is complete (or at least is expected to be complete). If separations are made, the separation factors are high (greater than 10^2).

In ion exchange chromatography, however, ions or molecules of similar behaviour are separated. The separation factor is usually low.

The third field of application of ion exchangers is their use as carriers. Ion exchangers saturated with certain reagent ions, enzymes, etc. can be used as stable reagents. Sometimes the ion exchanger acts as a carrier, on which the reaction takes place.

Certainly, there are many other applications. However, those most frequently and widely used belong to the three classes mentioned. Since the requirements in each of the three fields are different, it is useful to treat them separately.

Because the analytical application of ion exchange membranes is limited and their use and operations are quite different from those above, they are not discussed here.

Although the use and purpose of application of liquid ion exchangers is, in most cases, similar to those of solid ion exchangers the operations carried out with them are different. It is therefore better to give the recommendations concerning the analytical applications of liquid ion exchangers separately.

Ion exchange operations need accompanying exact measurement steps, even in those cases where they are the most important steps of the analytical method. Therefore the methods or instruments applied must be in full accordance with the conditions and quality (precision, accuracy and rate) of the ion exchange operations.

I. ION EXCHANGE OPERATIONS BASED ON TOTAL EXCHANGE (SIMPLE ION EXCHANGE OPERATIONS)

Almost all ion exchange methods belong to this class where, independently from the aim of the process, a certain ion(s) is to be adsorbed quantitatively (or partially), or exchanged stoichiometrically for other ions from solution.

- (1) In papers describing an ion exchange method the aim of the operation (separation of interfering substances, purification, enrichment, salt splitting, decreasing of the amount of matrix components) and the predicted ion exchange reaction taking place between the solution should be given first.
- (2) The type of ion exchanger recommended (resin or inorganic) should be given.
- (3) Specify whether a column or batch method and single or multiple extraction procedure is preferred for solid and liquid ion exchanger, respectively.
- (4) Characterisation of the solid ion exchanger.

The following facts should be given:

a, Classification according to operation (cation-, anion-exchanger, amphoteric-, chelate resin, etc.)

b, chemical description of the matrix: styrene-divinylbenzene copolymer; cellulose, dextrane or silica based, inorganic, etc.

c, type of the matrix: macroporous, gel type, isoporous, micro-crystalline, superficially porous or porous layer

d, characterization of the cross-linking of the resin: the nominal DVB content of styrene-divinylbenzene copolymer based resins, etc.

e, name of the functional groups (sulphonic acid, carboxylic acid, quaternary ammonium type, imino-diacetic acid type, etc.). If the ion exchanger is not monofunctional, all the types of group should be mentioned

f, the full commercial name, designation and source of the ion exchanger used. If the ion exchanger is not commercially available then a detailed description of the preparation should be given.

g, form of the ion exchanger particles: beads or granules.

h, particle size of the airdried ion exchanger. Preferably the upper and lower size limits not just the mean diameter should be given in mm, or B.S.S. Standard mesh.

i, capacity of the ion exchanger in equivalents (moles of monovalent ions) per dm^3 swollen bed or per kg dry (or airdried) substance units. The exact description of the method of determination of the capacity or the source of the prescription used should be given.

(5) Preparation and characterization of the column if column operation is used:

a, preliminary treatment of the ion exchanger (swelling, washing, treatment with acid or alkali solutions, rinsing, etc.). Details of concentration, temperature and time data.

b, column hardware along with all the necessary data. (Commercial or custom made, glass, plastic or metal; water jacket; connecting valves, etc.). If it is not of the usual designs a figure is recommended.

c, preparation of the ion exchange column (prepacked or the process of filling the tube). If a solution and not a pure solvent was used for the preparation then the composition of the solution is also important.

d, size of the ion exchange column. The length and the diameter of the settled ion exchange bed is to be given!

(6) If a batch rather than a column method is used then the preliminary treatment of the resin must be given in detail. (cf. 5.a.).

(7) A detailed description of the preparation and treatment of the original sample investigated. Sample size, dissolution procedure, permitted volume of the solution prepared, adjusted final volume, etc.

(8) Description of the ion exchange procedure. If a column method is used then

a, the preliminary treatment of the column. The composition, the amount (volume), the temperature and the flow rate (in dm^3 per hour) of the solutions used. Similar data on rinsing, the procedure for checking equilibration (e.g. pH measurement, etc.) or for complete washing, are also necessary.

b, at the description of the ion exchange procedure the lower and upper limits of the volume of the sample solution applied to the column is required. It is also very important to specify the temperature and flow rate. The composition, temperature and flow rate of the liquid used in the washing or rinsing steps completing the main procedure are also necessary.

c, If adsorbed ions are to be determined then the elution procedure must also be described in detail: composition, temperature (in the column), flow rate and volume of the effluent collected.

If a batch method is used then a detailed description of the ion exchange procedure (mixing, resin-liquid ratio, contact time, temperature, removal of the ion exchanger, rinsing etc.) should be given.

(9) If the substance in question is to be adsorbed or removed quantitatively from solution then it must be verified from the results of model experiments that the ion exchange of the ions or molecules in the sample is quantitative under the conditions given. The interferences of other possible substances should also be given. Suggestions as to the preliminary separation or washing of interfering ions and molecules should be given.

To verify the ion exchange method presented the results of model experiments carried out with a fixed volume of solution, but of different composition (containing various but usual components) should be given and the amounts of foreign ions or molecules that can be tolerated tabulated.

(10) The complete regeneration procedure including the preparation, volume, flow rate and temperature of the solutions used, and the method of controlling its completeness should be given. If the ion exchanger can be decomposed or spoiled during the main process or regeneration then the loss in capacity should also be mentioned.

(11) The complete analytical method including ion exchange should be compared to other methods used for similar purposes and the advantages and possible disadvantages of the method emphasised. The comparison should be extended to include precision, accuracy, time consumption, reliability, concentration range using numerical data. The lower and upper limits of the amount of the substance within which the determination can be carried out with suitable accuracy should be specified.

(12) The basic new principle or idea that makes the new method superior to earlier techniques or procedures should be clearly stated.

(13) If the main ion exchange reaction is unusual and can not be understood simply because of e.g. extra chemical reactions (complex formation, etc.) and the quantitateness of the reaction is important for complete ion exchange then the reactions should be clarified and the conditions selected verified by experimental results.

(14) If a batch method is used the correct amount of ion exchanger and the volume of the sample solution treated must be given. Since batch ion exchange is never complete (but in certain cases can be accepted as practically quantitative) the permitted limits of resin to sample solution volume ratio, and the permitted composition of the solution should be clearly given. Because interfering ions are much more serious in the batch method than in column operations (since interferences can be overcome here by the use of longer columns) the amounts of foreign ions that can be tolerated must be given.

II. SEPARATION AND DETERMINATION OF INORGANIC OR ORGANIC SUBSTANCES BY ION EXCHANGE CHROMATOGRAPHY

Ion exchange chromatography is used if at least two ions or molecules of similar chemical character are present. It can be used successfully to analyse very complicated mixtures containing many components of similar behaviour.

For quantitative analytical purposes elution column chromatography is mainly used. This procedure ensures the clear separation and separate determination of the components. The use of displacement or frontal chromatographic methods is limited.

Other widely used methods are the thin-layer and paper ion exchange chromatographic techniques, which also can be used for the separation and detection of components of complex mixtures. Because column and layer techniques have different requirements they are treated separately.

A/ Methods using ion exchange column chromatography

The important and essential information concerning new methods is as follows:

(1) Characterization of the chromatographic process according to the funda-

mental step or effect believed to control the distribution of the components between the two phases. (Ion exchange, ligand exchange, ion exclusion; salting out chromatography, etc.)

(2) Characterization of the ion exchanger used.

The following facts should be given:

a, classification according to type (cation, anion exchanger, amphoteric-, chelate forming, etc.)

b, classification according to the structure of particles: resin beads, surface coated glass beads, superficially porous beads or beads with chemically modified surface, etc.

c, chemical composition of the ion exchanger beads (granules) or surface layer: matrix and functional groups.

d, if resin beads are used, the character of the resin (macroporous, gel type) and the degree of cross-linking should be given.

e, full commercial name, designation and source of the ion exchanger used and specified above. If it is not commercially available, a detailed description of the preparation should be given.

f, form of the particles (beads or granules, etc.)

g, particle size, and particle size distribution. The extent of homogeneity of the particle size is very important, because it greatly influences the efficiency of the column prepared.

h, the capacity of the ion exchanger in milliequivalents (millimoles of monovalent ions) per cm^3 bed or per g dry substance. The description of the determination should be referred to or given.

(3) Description of apparatus and column preparation necessary for repetition of the measurements. If the apparatus is a commercial one then its type and source must be given. Otherwise a detailed description of its construction should be given. If a gradient elution technique is used then all the data relating to the gradient producing device, connections, injection head, etc., should be given.

(4) Description of the experiments and description of the new procedure. For an exact description of the procedure the following must be specified:

a, the preparation of eluent

b, pretreatment and preparation of the sample

c, the method of column preparation (if not a commercial column)

d, the pretreatment of the column

e, the mode of introduction of the sample into the column and the volume of sample injected

f, all the important conditions of the elution process: temperature, flow rate (linear velocity?). In the case of gradient elution the exact form and parameters of gradient, etc.

g, The method of determination of the separated components: flow-through detector or fraction collection and individual determination.

h, The method of evaluation of the measurements. Standardisation of the method used. The standard deviation and possible errors of the determinations.

(5) The new principle, idea or technique by which the separation and determination presented differs basically from earlier methods and the advantages of the new method over the known techniques should be clearly stated. The comparison should cover all important aspects including:

- a, resolution
- b, concentration range (upper and lower limits)
- c, limits of detection of the components
- d, precision and accuracy of retention data
- e, precision and accuracy of the quantitative determinations of the components
- f, long term stability of the system
- g, duration of the separation (and determination)
- h, ease of separation
- i, decrease in sample pretreatment required etc.

(6) If there are points which need verification (column packing method yielding more efficient columns, higher selectivity by using new chemical reagents or ion exchangers, etc.) these should be proved by experiments comparing the new results and those obtained by other techniques or methods.

It should be kept in mind that the height of one theoretical plate itself is not an absolute measure of the value of the column, since it is the actual separation of the components in question which is of interest and this separation depends on other factors as well. The time required for the completion of a separation, the long term repeatability, precision and accuracy of retention data and component determinations are the factors to look for and estimate during the comparison process.

B/ Methods using ion exchange, thin-layer, or paper chromatography
The important and essential information concerning new method is as follows:

- (1) Characterization of the chromatographic process according to the fundamental step or effect believed to control the distribution of the components between two phases. (Ion exchange, ligand exchange, etc.).
- (2) Characterization of the ion exchanger layer or sheet used.
 - a, classification according to type (cation, anion exchanger, chelate forming, etc.)
 - b, classification according to the structure of the sheet (impregnated paper, ion exchanger layer with additives, etc.)
 - c, chemical composition of the ion exchange medium: matrix and functional groups.
 - d, full commercial name, designation and source of the ion exchange paper or layer, used and characterized above. If not commercially available, a detailed description of the preparation of the sheet should be given.
 - f, the capacity of the ion exchange paper or thin-layer in equivalents (moles of monovalent ions) per dm^2 or rather per kg of the active layer. If the paper is impregnated in the laboratory the mass ratio of the ion exchanger and the paper; if the thin-layer is prepared in laboratory the ratio of ion exchanger and the additives should be given together with the capacity of the ion exchanger itself.
- (3) A description of the hardware used: if the sheet is prepared in the laboratory a description of the equipment used for the preparation is necessary. The system used for development of the chromatograms should be described in detail (glass or plastic, size of the device and its figure, if necessary). If the chromatogram is evaluated by an instrument (e.g. densitometer) then its designation and source should be given.
- (4) Description of the experiments and description of the new procedure. For an exact description of the procedure the following facts must be specified:

- a, the preparation of the developer (eluent) solution
- b, the preparation of the sample solution
- c, the pretreatment of the ion exchanger sheet
- d, the volume and mode of introduction of the sample onto the layer
- f, all the important conditions of the development: temperature, atmosphere, time, treatment of the chromatogram after development
- g, mode of detection, preparation of the detecting reagent (if any)
- h, the mode of the detection (Spraying of reagent(s), and measurements (densitometric measurements; using u.v. lamp or monochromatic light source; measurement of the light intensity of fluorescence; dissolution (recovery) of the spots followed by the individual determination of the components by infrared, u.v. spectrophotometry, etc.)
- i, the method of evaluation of the measurements (that of R_f , the quantity of the components): internal standards, etc. The accuracy and precision of the determinations, batch to batch and long term reproducibilities. Possible errors and interferences.

(5) It should clearly be stated by what new principle, idea or technique the separation and determination developed differ from earlier ones. What the advantages or possible drawbacks of the new method are. The comparison should cover all the important terms: resolution, concentration range, concentration ratio of the components, lower limit of interference, limit of detection, precision and accuracy, duration of a determination. To verify the statements comparison of numerical data obtained by the new and the known methods should be given.

III. ION EXCHANGERS USED AS CARRIERS IN ANALYTICAL CHEMICAL PROCEDURES

The purposes of the use of ion exchangers as carriers may differ: detection of certain components, estimation of their quantity; quantitative determination of components; preparation of reagent and so on.

In the paper describing a new analytical method using ion exchangers as carriers the following information should be given:

- (1) The aim of the use of an ion exchanger
- (2) The characterization of the ion exchanger (See Part I. point (4))
- (3) Preliminary treatment of the ion exchanger (pulverisation, swelling, washing, treating with acid or alkali solutions, rinsing etc.). Details of concentration, temperature and time data.
- (4) Description of the procedure involving the ion exchanger. Details of concentration, temperature, time data, preparation of solutions etc.
- (5) Description of the detection, estimation or quantitative determination step.
- (6) The basic new principle or idea that makes the new method superior to earlier techniques or procedures should be clearly stated. The comparison should cover all important terms with numerical data: limit of detection, concentration range, concentration ratio of components, selectivity, precision and accuracy (if quantitative determinations are made), duration of the procedure, stability of the reagent prepared etc.

REMARK

Concerning the terms used in each part of this report (Part I-III) the IUPAC recommendations for publication of new analytical methods (1), the recommendations on ion exchange nomenclature (2), and the recommendation on nomenclature (3) for chromatography (Part II) should be considered.

REFERENCES

1. R.W. Fennell, T.S. West, Pure Appl. Chem. 18, 437 (1969).
2. Recommendations on ion exchange nomenclature. Pure Appl. Chem. 29, 617-624 (1972).
3. Recommendations on nomenclature for Chromatography. Pure Appl. Chem. 37, 445 (1974).