

## TUBULAR ELECTRODES AND OTHER DEVICES FOR POTENTIOMETRIC DETECTION IN FIA

Isabel M. P. L. O. Ferreira and José L. F. C. Lima#  
Departamento de Química-Física  
Faculdade de Farmácia da Universidade do Porto  
Rua Anibal Cunha 164, 4000 Porto, Portugal

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### ABSTRACT

This paper examines potentiometric detection in FIA from the viewpoint of using either ion-selective electrodes (ESI's) or other electrodes which cannot be classified as such. We refer to the various ways of attaching the electrodes to the manifolds in conventional assemblies and describe the different designs for potentiometric detectors when these are expressly built to be incorporated in FIA manifolds. Particular mention is made of tubular-shaped electrodes and their potentialities in set-ups where detectors are placed sequentially.

### INTRODUCTION

There are several reasons which explain why flow injection analysis (FIA) [1] have become a widespread automatic analytical method. This is essentially due to the simplicity and low cost of the set-ups, their versatility and ease of assembling, and the resultant savings which make FIA accessible to all analytical laboratories. Hence, FIA is used as a detection process with practically all instrumental analytical methods, even though colourimetry and potentiometry predominated in Ruzicka and Hansen's first work.

The ease with which a cell with a small optical volume can be attached to a spectrophotometer, the effective manner by which one can link it up to the remaining FIA set-up, together with the existence of reasonably specific colour reactions (many of which are the basis of widely-used reference procedures), have so far ensured that colourimetry is the most frequently-used FIA detection process.

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#Author to whom correspondence should be addressed.

Regardless of the initial work on potentiometry as a detection process [2], its use did not become as widespread as that of colourimetry. This is most likely the result of the difficulties in attaching conventional ESI's to the flow system, for example in cascade arrangements, which discouraged laboratories from using them for routine determinations.

In spite of initial difficulties, there can be no doubt as to the advantages of potentiometric detection. [3,4]. In effect, it can frequently add to the well know advantages of the classic potentiometry, certain others resulting from combining ESI's and a FIA manifold.

Hence it is not surprising that today we can note the development of FIA manifolds with potentiometric detection that use the most diverse types of electrodes (Table 1), as well as the most varied geometric shapes and methods for attaching the electrodes to the manifolds (Table 2).

Table 1- Types of electrodes used in FIA potentiometric detection

Crystalline electrodes	5-53
Rigid matrix electrodes	44, 54-61
Electrodes with a mobile carrier	2, 45-49, 62-105
Sensitized ion-selective electrododes	51, 106-108
ISFET	109-116
Redox electrodes	117-118
Electrodes of the first kind	119-122
Electrodes of the second kind	49,52,53, 123-144

Table 2- Detector design and manner of attachment to FIA manifolds

Cascade arrangements	2, 6, 8,11,17, 18, 28, 42, 52, 54, 63-65, 69, 124
Flow-through caps	10, 12,14, 16, 18, 22-24, 26, 33, 38-41, 43-45, 48, 50,51,55, 61, 62, 74, 75, 82, 84, 87-89, 97, 104, 106-108, 111, 112, 114,116, 121, 123, 125,
Membranes with a filter paper	3, 4, 21
Wires inside the system	80, 81, 83, 86, 90, 98,117, 119-122 ,140, 143
Wall-jet design	9, 15, 19-21, 25, 27, 31, 34, 35, 37, 49, 53, 94, 101, 109, 110, 115, 118, 132, 143
Tubular shapes	5, 7, 13, 29, 30, 32, 36, 47, 56-60, 66-68, 70-73, 76-79, 84, 85, 91-93, 95, 96, 99, 100, 102, 103, 105, 113, 126-131, 133-139, 141, 142, 144

## TYPES OF POTENTIOMETRIC DETECTORS

The majority of electrodes which have so far served as the basis for establishing potentiometric detection systems for FIA may be classified as ESI's according to IUPAC recommendations [145], being about 66% those which incorporate crystalline membrane and mobile carrier electrodes. There is also a significant number of FIA manifolds whose detectors cannot be considered as being included in the aforementioned classification, namely electrodes of the first and second kind (Fig. 1)

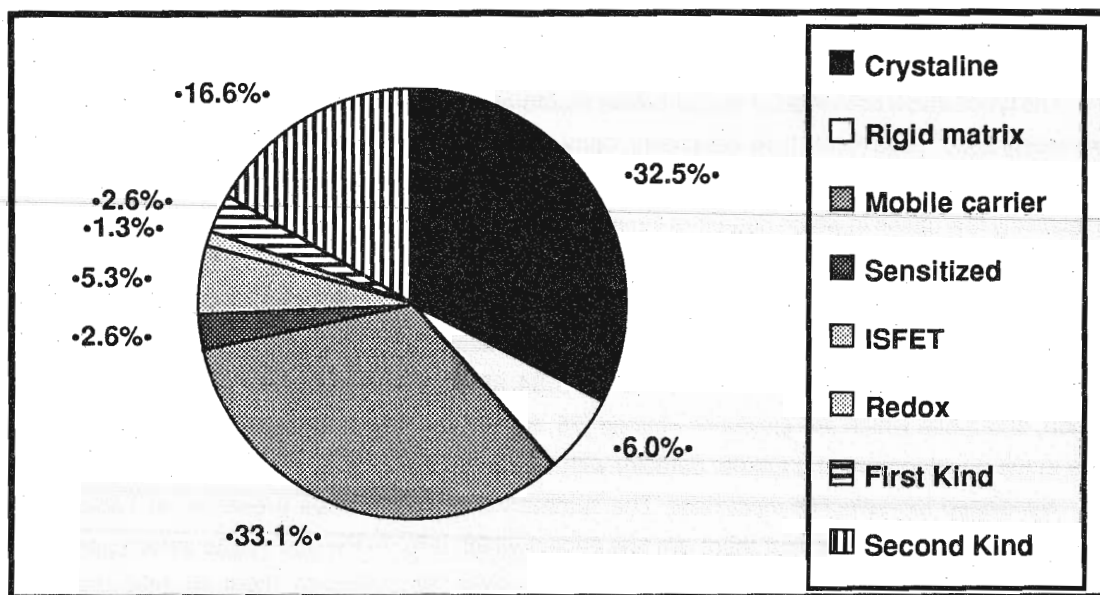


FIG. 1 - Distribution of types of electrodes used in FIA potentiometric detection (referred to October 1992)

*Crystalline membrane detectors.* This type of detectors, together with those based on mobile carriers, are the more widely used. In the majority of cases, commercial ion-selective electrodes with a homogeneous crystalline membrane are used in which the fluoride electrode predominates [6, 8-10, 20, 21, 24-27, 31, 33-35, 37, 40, 47, 49, 53]

Few are the cases in which the crystalline membrane is prepared expressly for its incorporation in a unit dedicated to FIA determinations. The majority of approaches utilize devices to fix the position of the conventional ion-selective electrodes and to restrict the flow of the solution across their sensing surface, namely those arranged as cascades [6, 8, 11, 17, 18, 28, 42, 52], as wall-jets [9, 15, 19-21, 25, 27, 31, 34, 37, 49, 53], or as flow-through caps [10, 12, 14, 16, 18, 22-24, 26, 33, 38-41, 26, 33, 38-41, 43-45, 48, 50, 51] which are similar to those used since the appearance of the first ESI's in continuous control [146, 147].

In the majority of cases in which crystalline membrane detectors were built with a view to their incorporation in FIA systems, the authors attempted to construct them in a tubular shape [5, 7, 13, 29, 30, 31, 36]. In some cases they resorted to the use of heterogeneous crystalline membranes [29, 30, 32].

*Rigid matrix detectors.* It is not surprising that this type of detector is rarely used in FIA (see Fig. 1) as only glass membranes sensitive to the proton present good operating characteristics. In the majority of cases which refer to their use, these are commercial tubular electrodes that are frequently used for continuous flow.

*Mobile carrier membrane-based detectors.* These, together with crystalline membrane detectors, are those most widely employed. They also frequently appear in set-ups in which conventional mobile carrier electrodes are arranged as a cascade [2, 63-65, 69], as a wall-jet [49, 94, 101], or as a flow-through head [45, 48, 62, 74, 75, 82, 84, 87-89, 97, 104]. Here, PVC is almost exclusively used to immobilize the sensor solution.

The types involved in trials of mobile carrier membrane detectors are predominantly those for which more widely used ESI's of this type are known, namely for calcium [45, 46, 62, 65, 66, 72, 79, 82, 89, 90], potassium [2, 46, 47, 49, 69, 70, 88, 90, 94, 101], and nitrate [2, 63, 64, 66, 73, 75, 77, 90, 92, 102]. There are relatively few cases in which detectors sensitive to organic species have been developed [66, 78, 85, 96, 99, 100, 103, 105].

It is regarding to detectors with mobile carriers that it can be found the most research directed at developing configurations expressly for FIA manifolds, namely tubular arrangements with [66, 67, 68, 70, 71, 72, 76, 77, 78, 91, 92, 93, 102] and without [73, 79, 84, 85, 95, 96, 99, 100, 103, 105] an inner reference solution, and those which are sandwich-shaped [75, 84, 97]. Of the various designs, reference is even made to the development of a tubular detector with a liquid sensor [66].

*Sensitized ion-selective electrodes.* The summary of the references presented in Table 1 could enable us to easily conclude that there are few papers which refer to the use of gas sensing electrodes or to enzyme substrate electrodes directly fixed to the system. Nevertheless, there are references in the literature to FIA manifolds that, generally speaking, are based on the same principle as that of the sensitized ion-selective electrodes. These set-ups either use a gas that is generated inside and later transformed into an ionic species that is measured by the detector [67, 68, 91-93, 95, 102, 113, 121, 125], or an enzyme to produce a species to which the ESI is sensitive [56-60].

*Ion-sensitive field effect transistors.* From the first paper that deals with FIA manifolds with ISFETS's attached [109] references were made to the possibility that this combination may be beneficial because the detectors can be easily miniaturize and more specifically, they may reduce dispersion in the measuring zone, present greater response rates, and improve the signal-to-noise ratio. The importance of the miniaturization is noted and stressed in several later papers [110-113].

We also note that FIA methods themselves also contribute to reducing some operating constraints still present in ISFET's [115], namely drift [112, 113, 115, 116] and the need for periodic calibrations [114], as well as offering the possibility of storing the electrode in conditioning and cleaning solutions for long periods of time [112, 114, 115].

*Redox electrodes.* Actually, when this type of electrodes is used in the conventional manner their use is almost exclusively limited to that of indicator electrodes in redox titrations. There is only one study

assessing their applicability as FIA detectors and the effects of different configurations on the quality of the signal they emit [117]. Yet another paper [118] examines the influence of various materials (platinum and graphite) as well as their usefulness in a determination in which the same type of electrodes were also used several years earlier as detectors in a segmented-flow system [148].

*Electrodes of the first kind.* As is the case with redox electrodes, there are few references in the literature to electrodes of the first kind as FIA detectors. In the cases referred the electrodes are made of copper [119-120] or silver [121-122] inserted into the set-ups in a wire-shaped [119-122].

*Electrodes of the second kind.* Considering that today this type of electrode is rarely used for batch procedures and alternatively there are good quality ESI's for the species to which they are sensitive, a surprising number of references to FIA manifolds with electrodes of the second kind can be found, regarding which there is a predominance of halide-sensitive units [49, 52, 53, 123-129, 132-134, 138-140, 142]. Here we note the numerous papers published by Van Standen [126-131, 133-137, 139, 141, 144] and Trojanowicz [49, 52, 53, 123, 124, 140] where these authors point to their potentialities and to those situations in which they could be useful for analyses of real samples.

This rehabilitation of the second kind electrodes is a result of the manner by which FIA determinations are carried out, namely due to the fact that the carrier liquid flows continually inside the indicator electrode, thereby systematically cleaning and conditioning it, and also because the measurements are performed within a fixed time after the sample is introduced into the system. These measuring conditions can compensate for the difficulties which are usually felt when the conventional electrodes of the second kind are used in direct potentiometry what is a similar situation to that referred previously for the ISFET's. Nevertheless, these detectors still present drawbacks typical of the second kind electrodes which restrict their use in certain cases such as bromide [134] or sulphide [135] determinations where the introduction of a dialysis membrane avoid any direct contact between the sample plug and the sensing surface [127].

## DESIGN AND ATTACHMENT

Generally speaking, the potentiometric detectors used for developing FIA manifolds can be divided into two groups: those which use in the majority of cases commercial available conventional shaped ESI's, or those devices which have been expressly constructed to be attached to the set-ups. Whichever the group, the literature refers to numerous variations of both.

When conventional electrodes are employed, they are predominantly attached to the set-up in the form of a cascade or wall-jet arrangements, or even with small devices to the end of the electrodes to limit the volume and flow of the solution which comes into contact with the sensor membrane (flow-through caps). Approximately 53% of the papers examined herein refer to one or another of these three types.

In those cases in which the detector is expressly built to be incorporated in a FIA manifold, there is a clear tendency to give them a tubular shape, and this type represents more than 36% of the cases referred to in the literature (Fig. 2).

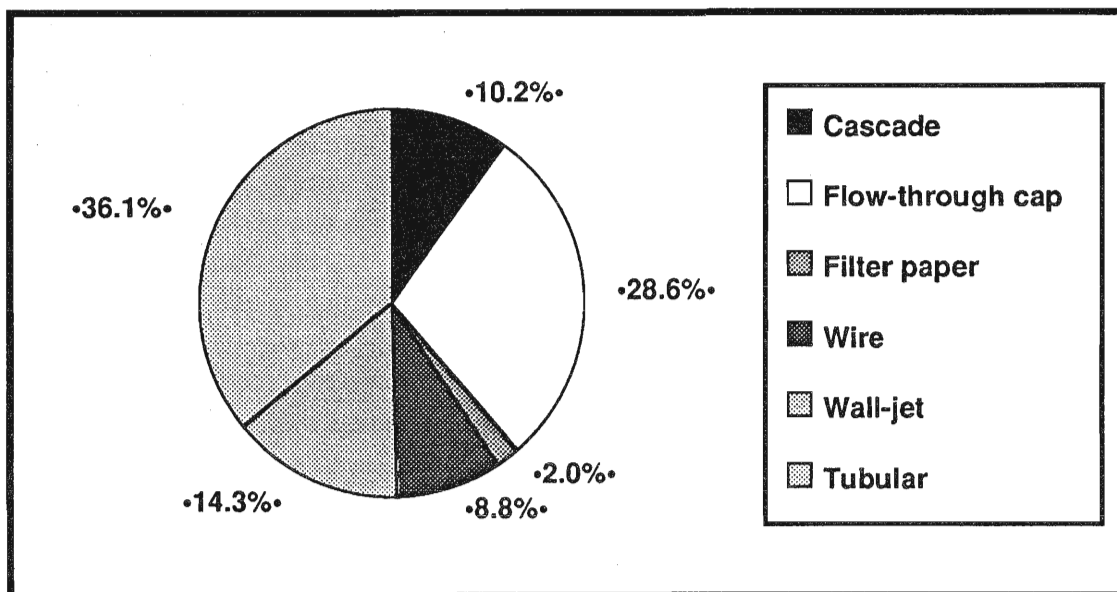


FIG. 2 - Distribution of the detector design and manner of attachment to FIA manifolds (referred to October 1992)

*Cascade arrangements.* This is the arrangement designed by Ruzicka and Hansen [2, 63-65] in their first papers in which potentiometry was used as FIA detection process. In this type of set-up a sample plug is prepared and carried through the manifold and it is only as it leaves this that it encounters the indicator electrode (or electrodes) flowing over the sensing surface. It then continues along to flow freely over the reference electrode or to a waste vessel whilst also establishing an ionic junction with the reference electrode.

Although right from the beginning these cascade arrangements bore out the usefulness of potentiometric detection in FIA, they also presented certain drawbacks mainly as regards their routine use by less experienced operators. The difficulties are essentially a result of the mechanical instability of the set-ups to which we can add the relatively prolonged contact of the sample plug and the carrier with the environment.

In earlier papers, other authors (see Table 2) used this type of arrangement for their work, sometimes with modifications, namely in placing the indicator and the reference electrodes face-to-face [6, 17] so that the solution would flow between the tips of both. This arrangement allows a better control of the membrane surface into contact with the carrier and the sample plug and also create a good mechanical stability for the ionic junction between the indicator and reference electrodes.

*Flow-through caps.* The use of devices that could be slotted in at the tips of conventional ESI's so that a continuous flow could pass over their sensing surface is almost as old as the ESI's themselves [146.147]. The use of these classical devices that were not expressly designed for attaching ESI's to FIA manifolds must be considered with caution. The dilution chamber which frequently was created at the tip of the electrode and which is perfectly acceptable for continuous flow determinations would, in FIA, cause an increase in the limit of detection of the determinations and a decrease in the sampling rate. In effect,

this type of device, expressly designed for FIA use and with a cell volume of about 15 $\mu$ L, is available on the market today [149].

We can also include the so-called "sandwich detectors" [75, 84, 97] in this group, in spite of their apparently different general appearance and the fact that they may even house the reference electrode itself. In effect, these devices consist of two pieces placed side-by-side in which one contains the sensor membrane and the other conditions the spread of the flow over the sensing surface.

*Membranes with a filter strip.* This type of detector is considered separately as it presents at the same time some of the characteristics of the cascade-type and of the flow-through cap detectors [3, 4, 21]. In effect, the position of the electrodes after the manifold does not differ greatly from the cascade arrangement. They include however a filter paper strip which controls the flow of the solution over the membrane and mechanically stabilizes the ionic junction with the reference electrode. This is a simple device that on the one hand obviates the need to purchase or build a flow-through cap whilst on the other hand, eliminating the typical problems that cascade arrangements create by the undefined spread of the solution flowing freely over the sensing surface.

*Wires inside the system.* Electrodes with a filiform active surface have so far been used in two ways: either encased in a microconduit circuit [80, 81, 83, 87, 122] or located in the centre of the stream [117, 119, 120, 122, 140, 143]. The composition of the sensing surface varies considerably as it may consist simply of platinum [117], copper [119, 120], or silver [121, 122], or even be lined with silver halides [122], silver sulphide [143], or a PVC film with an immobilized mobile carrier [80, 81, 83, 87].

*Wall-jet design.* In this type of cell design, the solution spreads uniformly over the entire membrane, creating a minimal diffusion film thickness. When the rate of flow and the distance between the inlet nozzle and the sensing zone is properly selected, back-mixing is minimal. The wall-jet design is predominantly used with commercial ESI's and most especially with electrodes that are sensitive to the fluoride anion [9, 20, 21, 25, 26, 27, 31, 34, 35, 37, 49, 53].

Given that a potentiometric detector for FIA must present a rapid response rate, good wash conditions, as small a dead volume as possible, be easy to use and maintain, inexpensive and accessible to all, one can easily conclude, as Frenzel states [31], that generally speaking, wall-jet arrangements may, to a certain extent, satisfy all these conditions. We must not however forget that the way by which these operate destroys the sample zone thus barring their use in set-ups where the detectors are placed sequentially (except when placed at the end of the line). Moreover, the behaviour of the wall-jet detectors also rules these out in set-ups which use the stopped-flow technique.

Various detailed studies on the working characteristics of the wall-jet detectors [31, 34] when comparing them to other types of potentiometric detectors, frequently stressed certain advantages such as their response rate and the stability of their potentials.

*Tubular electrodes.* Today the tubular shape seems to be the preferred design for potentiometric detectors as recently expressed [150] and was been used in approximately 36% of all the papers reviewed in this study.

This preference is justified by the advantages that tubular detectors present as compared to other types and which greatly increase the potentialities of the potentiometric detection, namely as regards multiparametric determinations. In the majority of cases, the entire detector has to be especially built if

these detectors are to be used in FIA manifolds, as opposed to the other types discussed herein where, for example, conventionally shaped electrodes are employed without any modifications or with just a few simple adjustments.

The preparation of a tubular detector depends greatly on access to a sufficiently versatile construction process which can fashion the electrode to the desired shape. This limitation no doubt explains why it has taken several years for this type of potentiometric detectors to become generally used. This is illustrated, for example, by the fact that there are various references to the use of electrodes of the second kind for the determination of halides [49, 52, 53, 123-129, 132-134, 138-140, 142] and that few papers refer to the use of crystalline membranes sensitive to these ions [7, 13, 30, 32, 36]; in two of these a heterogeneous crystalline membrane is actually used [30, 32].

There are more numerous general construction procedures for tubular detectors based on membranes with a mobile carrier (and the corresponding variations). There are essentially two types of set-ups for this type of detectors: those which employ inner reference electrodes and solutions, and those in which the sensing membrane is directly attached to a conductive support.

The type of construction suggested for tubular detectors with inner reference electrodes and solutions may be that of a wall which is totally lined by the sensing membrane, as proposed by Moody and Thomas [72], or only partially lined as proposed by Meyerhoff [67, 68, 70, 71, 77, 78]. Whichever the case, the area of the tube whose wall consists of PVC and an immobilized sensor, is surrounded by the reference solution in which an AgCl/Ag electrode is immersed and used as an internal reference.

The development of ESI's with a mobile carrier, in which the sensing membrane was applied directly on a support consisting of a silver-based conductive epoxy resin [151-153], which could be fashioned in the most diverse shapes [154,155], served as a basis for the design of tubular potentiometric detectors without an inner reference solution. Since the appearance of the first detector of this type sensitive to calcium [73], the construction process has been used to prepare detectors which are sensitive to a great variety of ions, as well as to organic species of pharmaceutical interest [96, 99, 100, 103, 105].

Originally the device consisted of a perspex support which holds a small hollow cylinder of the same material filled with an epoxy resin made conductive by silver or graphite and drilled lengthwise; the walls of this channel were covered with a PVC membrane. As time passed, the original design was modified several times in order to simplify handling, namely by incorporating in the same block an ESI with a homogeneous crystalline membrane as a reference electrode (Fig. 3).

The majority of references to tubular detectors sensitive to species for which we have crystalline membrane ESI's with good operating characteristics, are based on second kind electrodes. This apparently contradictory situation is doubtless due to the ease with which one can build a small silver, or other metal, tube whose inner wall is covered with a poorly soluble salt, and incorporate it in a FIA manifold.

Little reference is made in the literature to crystalline membrane tubular detectors built especially for FIA systems [5, 7, 13, 29, 30, 32, 36]. These use a direct contact with the membrane (absence of internal reference solution), either of the homogeneous [5, 7, 13, 36] or heterogeneous [29, 30, 32] type.

In a recent work of our research group, we developed a procedure for building homogeneous crystalline membrane tubular detectors (Fig. 4), following on the improvements made on earlier ones [36], that allows us to obtain detectors with working characteristics very appropriate for FIA systems. These



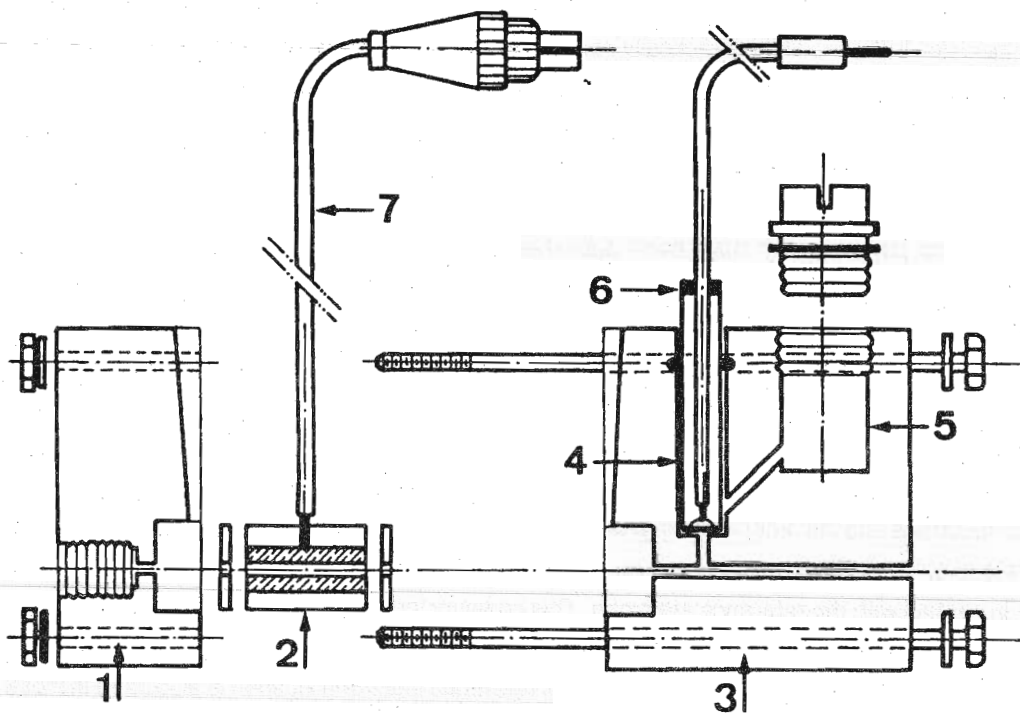


FIG. 3-Design of the tubular detector with a PVC membrane: (1) perspex support piece; (2) sensing unit with a PVC membrane; (3) perspex piece with reservoirs; (4) reference electrode reservoir; (5) electrolyte reservoir; (6) AgCl/Ag<sub>2</sub>S electrode; (7) shielded cable

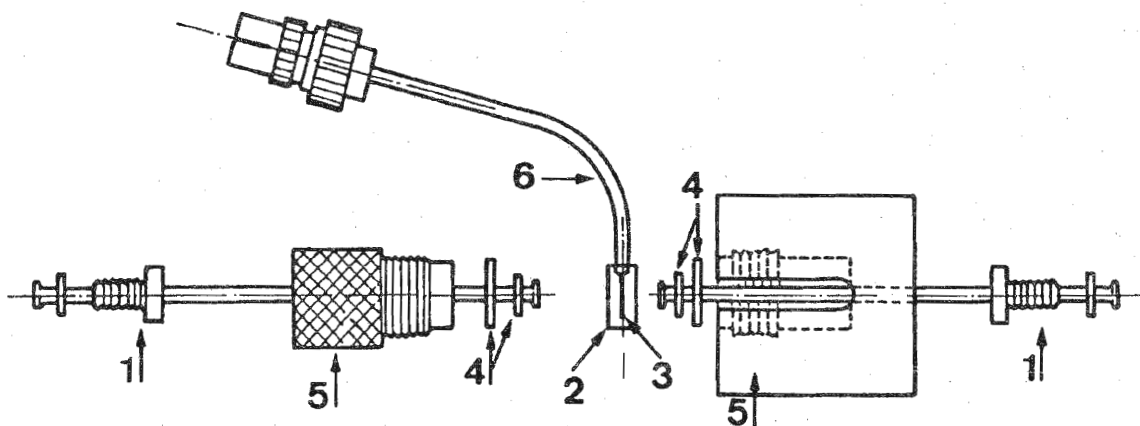


FIG. 4-Construction phases for tubular detector with crystalline membrane: (1) inlet/outlet threads; (2) sensing unit; (3) homogeneous crystalline membrane; (4) O-rings; (5) perspex thread holders; (6) shielded cable

units present excellent stability during large periods of time, a very fast response time, high sampling rates, and their inclusion in the manifolds practically does not distort the hydrodynamic characteristics of the flow, all of which makes them most attractive for manifolds with sequential detectors.

## PLACING AND ATTACHING THE REFERENCE ELECTRODE

Few of the papers which have been published on potentiometric detection in FIA go into detail regarding the type of reference electrodes and the manner by which they can be attached to the set-up, no doubt because in the majority of cases these are commercial reference electrodes and their mode of attachment deserves no special mention. In effect, in most cases the reference electrodes are placed at the end of the line in the container into which the solution drops or receive the solution directly as it leaves the manifold.

More complex are those set-ups in which the flow is first split up into two channels, one for the reference electrode and the other for the injection valve and the indicator electrode [7, 13, 72]. This process attempts to avoid that, during determinations, there is a periodic change in the composition of the solution which is in contact with the reference electrode. This however increases the complexity of the set-up and possibly diminishes the reproducibility of the output signals due to the need for maintain a constant split-flow throughout the determinations. A similar type of reference electrode location is also used in those set-ups which are based on microconduits.

The manner by which the reference electrodes are inserted and their location are crucial when one wishes to take full advantage of the potential of potentiometric detectors to develop manifolds with sequential detectors. In this case good results may be obtained by placing the reference electrode in a side canal with no flow of the solution [79]. This type of arrangement may also be used in manifolds designed for uniparametric determinations in order to obtain systems which are free from mechanical or electric problems [96, 99, 100, 103].

In the literature, one can also find the description of a set-up without a reference electrode in the sense that we have previously mentioned, that is, an electrode with a desirably constant potential. These set-ups use two indicator electrodes placed at a certain distance so that when one is in contact with the sample plug, the other is in contact with the carrier, and vice-versa [31]. In this manner the analytical signal appears amplified at the cost of the sum of the potential supplied by each of the two electrodes.

## FIA MANIFOLDS

The linking of ESI's to FIA manifolds is frequently aimed at overcoming the typical constraints of conventional potentiometric determinations by eliminating the decision-making factors which are attributed to the operators, namely as regards the stability of the potentials. As recent papers have stated, this choice is perfectly understood by all those who have already been confronted with the use of batch potentiometric determinations [4, 150, 156]. In effect, the operating characteristics of the electrodes can be improved by using these together with a FIA system, namely because of the systematic conditioning effect which may be produced by the carrier or even due to the improved values of the respective limits

of detection supplied by the same electrodes in batch procedures.

Hence one cannot be surprised by the frequency with which FIA manifolds with potentiometric detectors are used with the sole purpose of carrying the sample plug in a reproducible manner from the point of injection to the detector. Consequently, there is a predominance of the single channel or double-channel type, in which the auxiliary channel is employed for adding the solution used to adjust the pH or the ionic strength.

The more complex FIA manifolds are usually used to overcome some of the limitations which the use of potentiometric detectors may create, or to increase their analytical usefulness. Hence, we can find references to set-ups which use dialysis membranes to prevent the electrodes from entering into contact with complex matrixes or to diminish interferences [77, 78, 83, 127], preconcentration devices when the limit of detection of the ESI's proves to be insufficient [19, 28, 35], gas diffusion devices [14, 15, 67, 68, 71, 91-93, 95, 113], and even an isothermal distillation unit [55].

Even in the simpler FIA manifolds, the drift of the electrode potential is a drawback which leads to a decrease in the reproducibility of the results. In many cases one can minimize the problem of the drift by using a carrier solution in which the ion for which the electrode is sensitive is present in a small concentration. There are authors however who defend the idea that the drift does not become a major problem as long as one always measures the height of the peak from the baseline [4].

The drawbacks resulting from the use of detectors which present a potentials drift may be totally overcome, without increasing the complexity of the set-ups, as recently shown in determinations with an electrode sensitive to Vitamin B<sub>6</sub>. To do so, it is only need to substitute the classic six-port valve by an eight-port and four-way injection valve which makes it possible, with all injections, to place the sample plug between two standard solutions, one at a higher concentration and the other at a lower concentration than that of the species to be determined [103]. In this manner and with each injection, the detector is calibrated without significantly altering the sampling rate.

## CONCLUSIONS

The ESI's with the best working characteristics in conventional procedures are also those most frequently employed for FIA potentiometric detection. In effect, considering the group of detectors based on crystalline membranes and mobile carriers (only exceptionally not immobilized in PVC), these represent more than 66% of the papers studied herein. Hence, it is also not surprising that as regards crystalline membrane ESI's, the great majority of papers involve the detection of halides, whereas regarding the mobile carrier detectors, many papers are published on the calcium and potassium cations and the nitrate anion.

Albeit today there is a clear preference for tubular detectors, this trend would be more even noticeable if we were to examine only those papers published in the past three or four years.

There is a great predominance of papers in the literature of this area reporting on the construction and evaluation of potentiometric detectors and it is to be expected that their number will increase as considerable research in this field still remains to be done. For example, and considering that cadmium cation ESI's are commercially available, there is still no reference in the literature to the development of

a crystalline membrane detector sensitive to this species.

The usage of potentiometric detection in FIA manifolds for real sample analysis is an aspect which has been studied less and in many cases, the results obtained are presented in little detail, namely as regards the quality of the values obtained with the systems proposed. Furthermore, there are a few comparisons of results with other procedures for which FIA systems are presented as an alternative, more exactly, comparative evaluations with reference procedures.

There are mutual advantages to using potentiometry and FIA so that potentiometry cannot be seen as yet another detection process alternative for FIA. On the one hand, the FIA manifolds frequently become much simpler when they use potentiometric detectors, for example, they benefit from the consistent sensitivity of the ESI's for a wide range of concentrations thereby avoiding the need for great dilutions within the system. On the other hand, potentiometric detectors when incorporated in FIA manifolds prove to have better operating characteristics when employed under similar conditions in batch determinations, namely regarding stability, reliability, potentiometric selectivity coefficients and the limit of detection.

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