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Chemical speciation by sequential injection analysis: an overview☆

J.F. van Staden*, R.I. Stefan

Department of Chemistry, University of Pretoria, Pretoria 0002, South Africa

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Abstract

The simplicity of the sequential injection (SIA) manifold and its low need for maintenance makes it an ideal tool in speciation. As miniaturization and reduction of reagent consumption are also ultimate goals in chemical sensing, it is useful to review the use of combined injection and programmed flow as a central issue in designing SIA systems with chemical sensors and structurally simplified chemical analysers. This overview gives an insight into the current state, analytical scope and performance characteristics of sequential injection systems as analytical tools for speciation. The suitability of SIA for speciation analysis is illustrated by the methods used in the conduits of sequential injection systems for the chemical conversion of different chemical forms into detectable chemical species. Configurations of the basic sequential injection speciation analysis systems were designed around a multi-syringe-time-based-injection system with one detector, direct and indirect speciation of different forms using a single detector including diode array detection and direct speciation of different forms using multiple detection.

Examples showing the use of SIA for the simultaneous determination or speciation of metal ions, inorganic anions and organic compounds are given with some recent results from our research groups.

Keywords: Sequential injection; Miniaturization; Diode array detection

1. Introduction

In 2000 in a comprehensive document, the IUPAC gave guidelines for terms related to chemical speciation and fractionation of elements and defines speciation of an element as its distribution amongst defined chemical species and uses the terms speciation analysis and fractionation to refer to analytical activities [1]. The growing awareness of the strong dependence of the toxicity of elements upon their specific chemical forms has led to an increasing interest in the qualitative and quantitative determination of specific species. Therefore during the last two decades, many of the research groups involved in trace element analysis extended their field of interest from total element measurement to that of trace element species. This brought new insights into the properties of specific trace element compounds, the need to measure them accurately and the challenge to develop appropriate analytical techniques. Therefore speciation becomes necessary to understand the toxicity of elements and their biological activity, as many elements may exist in various chemical forms with contrasting and several different effects [2–6]. Speciation measurements are carried out for a number of reasons, including characterization and evaluation of systems in environmental science, medicine, biological process monitoring, forensic investigations, nutrition and industry. Biochemical and toxicological investigation has shown that, for living organisms, the chemical form of a specific element, or the oxidation state in which that element is introduced into the environment, is crucial. The importance of chemical speciation became evident in the large number of papers published for the past 2 decades in scientific journals and books [1–14].

One of the most difficult problems encountered in speciation analysis is the development of an analytical procedure that does not disturb the chemical equilibria between the different forms of the element that exist in a given matrix [15]. The determination of the total amount of all elements in a given material followed by computer-aided calculation

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* Corresponding author. Tel.: +27-084-480-7263.
E-mail address: Koos.vanStaden@chem.up.ac.za (J.F. van Staden).

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of the concentrations of particular species based on ionic and redox equilibrium constants should be the most satisfactory procedure [15]. The success of such a procedure is, however, limited due to the number of available data e.g., stability constants, the difficulties in taking into account all kinetic factors, adsorption and desorption processes, ionic strengths, polymerization reactions and heterogeneous processes. Therefore in normal routine analytical laboratories the most practicable procedures for the analytical determination of specific species in a matrix is dominated with the use of different separation operations, chemical conversion into detectable species and different detection methods [15].

The majority of methods in speciation analysis currently still include a separation step before detection of the different species. A recent literature survey revealed that high performance liquid chromatography (HPLC) [16–21] was the dominant separation technique with around 550 publications followed by ion chromatography (IC) [22–26] with around 240 publications. An interesting feature is that the main hyphenated techniques for speciation analysis still include HPLC-ICP MS as detection device. A number of comprehensive reviews on chemical speciation by flow injection analysis (FIA) have been published [15,27–30] and a recent literature survey revealed the publication of around 200 articles in peer-reviewed journals. In most of the FIA systems designed for speciation analysis the distribution of species in natural matrices have been done by simultaneous determination of species in different oxidation states, determination of the complexation degree of metallic elements or determination of the content of a given complex compound.

2. Speciation by sequential injection analysis

The introduction of the sequential injection (SIA) technique [31–35] broadened the scope of flow analysis for speciation analysis. SIA is a technique that has great potential for on-line measurements due to the simplicity and convenience with which sample manipulations can be automated. A general schematic flow diagram of a sequential injection analyser is depicted in Fig. 1. The versatility of the sequential injection technique is centered around a selection valve (SV) where each port of the valve allows a different operation to be performed. An important advantage of the SIA technique is the versatility that the multi-position valve provides [34–36]. Each port of the valve is dedicated to a specific purpose and the combinations of sample, standards, reagents and detectors around the valve are easily modified to suit a particular analysis. The basic components of the system are a pump with only one carrier stream, a single selection valve (SV), a single channel and a detector (D). The concept is based on the sequential injection of a sample zone (S) and a reaction zone(s) (R) into a channel [35,37–39]. In this way a stack of well-defined zones adjacent to each other is obtained in a holding coil (HC). After the valve has been selected to the detector position, the flow in the carrier stream is reversed and the zones mutually disperse and penetrate each other as they passed through a reaction coil (RC) to the detector (D). The flow reversal as a result of the injection step therefore creates a composite zone in which sample and reagent zone penetrate each other due to combined axial and radial dispersion. Controlled dispersion and reproducible sample handling [34,35,39,40] are integral and indispensable prerequisites for the success of SIA. Computer control of the SIA system is therefore an essential prerequisite [34,35,39,41] since an analytical procedure often requires a complex and high reproducible flow pattern. We may ask why do we choose SIA for speciation analysis? The main advantages are the simple manifold design, robustness, reliability with a low frequency of maintenance and that the consumption of reagents and samples are very low. SIA is ideally suited for multiple determinations due to its discontinuous nature and therefore for the manipulation of samples containing different chemical forms of species in a matrix.

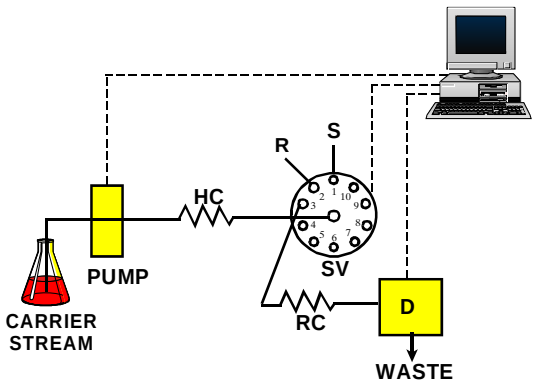

Fig. 1. Schematic flow diagram of a basic sequential injection analyser: S = sample; R = reagent; SV = selection valve; HC = holding coil; RC = reaction coil and D = detector.

A recent literature survey revealed that only a few publications appeared employing sequential injection for speciation analysis and that this field is still wide open for research. Among the methods used in the conduits of sequential injection systems for the chemical conversion of different chemical forms into detectable chemical species were kinetic discrimination, a time-based multi-syringe system, and confluence point after the selection valve with sample as carrier, sequential injection extraction and using the reduction and oxidation properties of different elements. So far configurations of the basic sequential injection speciation analysis systems were designed around a multi-parametric sequential injection system [42], direct and indirect speciation of different forms using a single detector including diode array detection and direct speciation of different forms using multiple detection. The basic schematic flow diagrams for the sequential injection analysis systems using single and multiple detection is depicted in Figs. 2 and 3 respectively.

The following parts are a more detailed description of the different sequential injection speciation configurations to date with a number of SIA speciation studies from our research group.

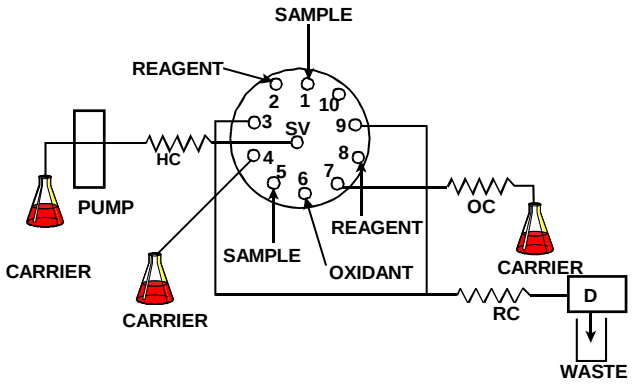

Fig. 2. Schematic flow diagram of the basic SIA system with a single detector used for speciation analysis: SV = selection valve; HC = holding coil; RC = reaction coil; OC = oxidation coil and D = detector.

3. Sequential injection configurations

3.1. Multiparametric sequential injection system

Thomas et al. [42] described a multiparametric sequential injection system for the speciation of different forms of nitrogen (ammonium, nitrites, nitrates and total nitrogen) and phosphor orthophosphates and total phosphor). The authors coupled their system with two spectrophotometric detectors where all the parameters were measured using either the direct exploitation of the UV spectrum of the sample, and a chemical reaction with one stable and simple reagent. One eight photodiode polyphotometer was used as SIA detector for the visible region and one 16 diode array for the UV region. They used a titration autoburette as liquid driver with a number of selection valves in their SIA system. For the determination of ammonium, sample and alkaline solution were sequentially aspirated into a holding coil, flow reversed to a donor shell of a gas-diffusion unit whereafter the ammonia diffused through a hydrophobic membrane into an acceptor shell containing an acid base indicator that was mixed and propelled to the detector for measurement at 640 nm. Nitrate determination was done with the modified Griess reaction where sample and Griess reagent were sequentially aspirated to a holding coil, mixed by flow reversal and transported to a detector for measurement at 530 nm. Total nitrogen was determined using UV radiation for digestion. Buffer, oxidant, sample, oxidant and again buffer were aspirated to a holding coil, stacking the sample zone sandwiched between two reagent and buffer zones followed by propelling the mixture to a UV reactor delayed for 3–5 min and transported through a UV detector for measurement. For the determination of orthophosphate the vanadomolybdate method was used where hydrochloric acid, reagent and sample were sequentially aspirated into a holding coil and there through flow reversal propelled to the detector for measurement at 430 nm. The same SIA manifold was used for the determination of total phosphorus, but with UV digestion.

3.2. Confluence point after selection valve-sample carrier

A flow system with in-line blank correction for the speciation of total iron and chromium(VI) in wastewater was described by Morais et al. [43]. The flow system uses the sample as carrier with a propulsion device situated after the single detector. The selection of sample or the reagent solution into the manifold is carried out by a eight-port selection valve. Therefore, the sample or sample/buffer solutions provide the baseline; the signal increment is due to the reagent intercalation. This approach allows the correction of the intrinsic color of the sample, as it provides baseline adjustment for each sample. A confluence situated just after the selection valve allows the sample composition to be adjusted for the color measurement. The flow system was applied to the colorimetric determination of total Fe and Cr(VI) in wastewaters between 0.1–6.0 and 0.03–1.0 mg/l, respectively with R.S.D. = $s < 3$ at a sampling rate of approximately 40 h.

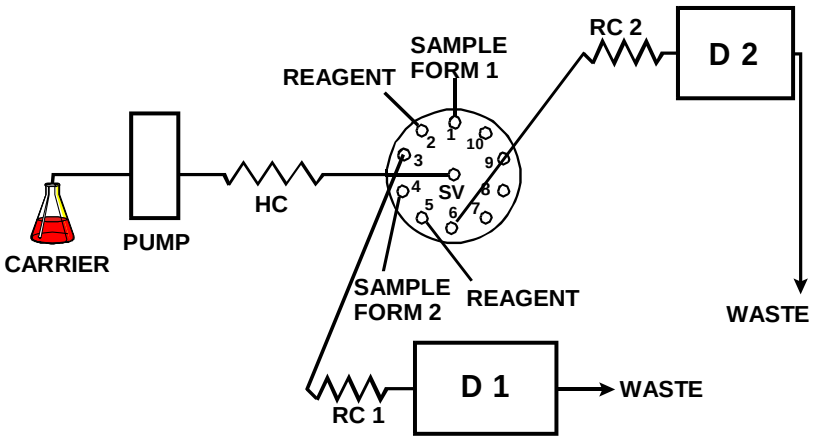

Fig. 3. SIA system for direct speciation of different forms using multiple detection: SV = selection valve; HC = holding coil; RC1 = reaction coil 1; RC2 = reaction coil 2; D1 = detector 1 and D2 = detector 2.

3.3. Using the oxidation and reduction properties of certain elements

A sequential injection system using the oxidation properties of iron(II) to iron(III) followed by measurement with single detector was described [44] for the quantitative discrimination of the two iron species, Fe(II) and Fe(III). Tiron was used as the chromogenic reagent for Fe(III) and total iron after Fe(II) was oxidised to Fe(III) by H_2O_2. The system operates by first determining Fe(III) with tiron, followed by the determination of total iron which also includes the resulting Fe(III) produced by the oxidation of Fe(II) to Fe(III) by hydrogen peroxide. The profile from this method displays two distinctive peaks for Fe(III) and total iron respectively. The Fe(III) forms a complex with tiron in a 1:1 ratio that was monitored spectrophotometrically at 667 nm. The concentration of Fe(II) was determined by subtracting the Fe(III) concentration from the total iron concentration. The linear range for this system is between 0.15 and 100.00 mg l^{-1} and 0.30–80.00 mg l^{-1} for Fe(III) and Fe(II) respectively with a % R.S.D. of 1.3 and 0.8 for Fe(III) and Fe(II) respectively. The detection limit was found to be 0.10 and 0.15 mg l^{-1} for Fe(III) and Fe(II), respectively. The system is fully computerized and able to run 30 samples h^{-1}.

Chromium speciation analysis has been performed by a large number of research groups using various techniques. The reason for this is that the two chromium species, chromium(III) and chromium(VI) differ enormously with regards to their biological and chemical properties and that chromium pollution originates from wastewater of metallic smelting, electroplating, hide processing and the dye stuff industries. It is therefore essential to discriminate quantitatively between the two, given that Cr(III) forms compounds that are essential trace elements in the human body playing a vital role in the metabolism of glucose and certain lipids mainly cholesterol while Cr(VI) compounds are very toxic and carcinogenic. The sequential injection system [45] uses a single detector and operates by first measuring the Cr(VI) species followed by the oxidation of Cr(III) to Cr(IV) by Ce (IV) and then measured the total chromium content. The spectrophotometric approach chosen relies on the specific reaction of Cr(VI) with diphenylcarbazide. The reaction occurs reliably in an acidic medium to give an intense red–violet complex cation that is monitored spectrophotometrically at 548 nm. The ligand reacts slightly with the other transition metals, but these complexes have a different colour to the Cr(VI) complex and this minimizes the risk of interferences during the spectrophotometric determination. The SIA system speciates between Cr(III) and Cr(VI) with an R.S.D. of better than 0.7% for both Cr(III) and Cr(VI). The frequency of sampling is 30 determinations per hour with a sample interaction of 1.1%. The linear range for Cr(III) is between 0.85 and 25 mg l^{-1} and for Cr(VI) between 0.16 and 20.00 mg l^{-1}. The detection limit is 0.042 and 0.023 mg l^{-1} for Cr(III) and Cr(VI), respectively. Statistical evaluation showed that the SIA system performed very well in comparison to the standard methods.

A sequential injection system using the reduction properties of Mn(VII) to Mn(II) followed by measurement with single detector was described [46] for the speciation of the two species. The reaction between PAR and Mn(II) was used followed by the subsequent spectrophotometric monitoring of the Mn(II)-PAR complex at 500 nm. The following sequence is followed in the procedure of the proposed SIA system. Mn(II) is first directly determined followed by the determination of the total manganese concentration after the reduction of Mn(VII) to Mn(II) by ascorbic acid. The sampling frequency is 30 determinations h^{-1}. The linear range for Mn(II) is 0.020–0.500 mg l^{-1} with a detection limit of 0.005 mg l^{-1} and for total Mn 0.025–0.550 mg l^{-1} with a detection limit of 0.008 mg l^{-1}. The % R.S.D. is 0.27 and 0.34 for Mn(II) and Mn(VII), respectively ($n = 10$). Chemical masking of Fe and Al was achieved by on-line addition of a 0.1 mol l^{-1} NaF solution. The proposed system yielded results that compare very well with standard methods.

Although very important in the biological an environmental cycle, little has been done on the speciation of bromine and bromide. We used the oxidative properties to oxidised bromide to bromine in the sequential injection speciation of bromine and bromide with spectrophotometric detection [47]. An on-line procedure for the simultaneous determination of bromine and total bromine (bromine + bromide oxidised to bromine) is described, which lead to the determination of bromide by subtraction. Phenol red was used as chromogenic reagent for bromine and total bromine after bromide was oxidised to bromine by Chloramine T. The linear range found is 1–10 mg l^{-1} with a detection limit of 0.6 mg l^{-1} for bromine, and a linear range of 0.8–15 mg l^{-1} with a detection limit of 0.4 mg l^{-1} for total bromine. The calculated R.S.D. for bromine is less than 0.8% and for total bromine less than 0.7%. The system is fully computerised and able to run 30 samples h^{-1} with an automated rinsing step that eliminates sample carry-over. The results for both bromine and bromide from the SIA system compare favourably with standard manual methods and statistical evaluation proves no significance between the results of the SIA system and the standard method at the 95% confidence level. The other halides do not interfere.

3.4. Speciation of organic compounds

The role of chirality has become firmly established in the drug industry. Worldwide sales of chiral drugs in single-enantiomer dosage forms continued growing at a more than 13% annual rate. The application of FIA/sensors or SIA/sensors systems for the speciation of enantiomers is specially needed to be developed for the pharmaceutical industry, due to the necessity to accurate and precise discriminate between the enantiomers of the drugs with a chiral center. The reason for such analysis is due to the difference in the pharmacokinetics and pharmacodynamics

of chiral drugs. Accordingly, for raw materials of the chiral drugs, an enantiopurity test must be performed.

The discontinuous nature of sequential injection analysis was also used for the direct speciation of different forms using multiple detection (Fig. 3). Two amperometric biosensors based on L- and D-amino acid oxidase, respectively, was used for the simultaneous detection of S- and R- captopril in a sequential injection analysis system (SIA) [48]. The linear concentration ranges are: 0.4–1.6 μmol l^{-1} (S-captopril) and 120–950 nmol l^{-1} (R-captopril) with detection limits of 0.2 μmol l^{-1} and 15 nmol l^{-1}, respectively. The biosensors/SIA system can be used reliably on-line in synthesis process control, for the simultaneous assay of S- and R-captopril with a frequency of 34 samples h^{-1}.

4. Conclusions

From the recent literature survey it is clear that the scope for sequential injection speciation analysis is still wide open. The discontinuous nature of sequential injection analysis with its robustness, simplicity, ease of operation, reliability, low reagent and sample consumption, convenience with which sample and reagents manipulation can be automated makes it ideally suitable for on-line process speciation analysis especially where process or environmental monitoring is necessary. It is sure that with the increase in speciation of the different chemical forms the trend for the development in SIA systems will also be in this direction.

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