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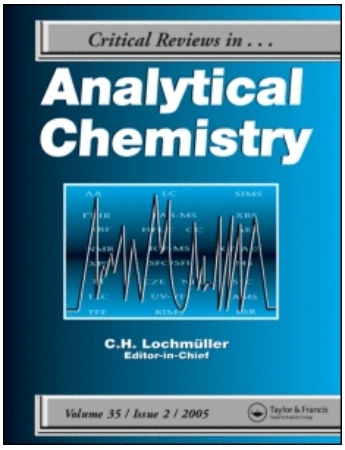

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Flow Injection, Overlooked Techniques in Forensic Analysis

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Flow Injection, Overlooked Techniques in Forensic Analysis

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Since their introduction in the mid-1970s, flow injection (FI) techniques have gained a worldwide popularity. FI techniques are automated, miniaturized, versatile, and inexpensive analytical tools for handling reagents and samples and consequently for conducting procedures related to wet chemical analysis. Due to their tremendous benefits, FI techniques have proven to be significant applications to such analytical fields as pharmaceutical, environmental, biochemical, and food. Currently, more than 10,000 publications reporting various applications of FI techniques can be retrieved from the literature. However, FI techniques have not yet received an adequate attention to the field of forensic analysis; less than 30 publications were reported.

The main objective of the current article is to draw attention to the potential of FI techniques to forensic analytical chemists. The article provides a comprehensive review of the applications of FI techniques to forensic chemical analysis, which covers the literature since the inception of the techniques. The article also offers a brief historical background on the developments of the generation and versions of the techniques while highlighting their advantages. In addition, future perspectives in the applications of FI techniques to forensic analysis are discussed.

Keywords forensic analysis, flow injection analysis, sequential injection analysis, bead injection analysis

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INTRODUCTION

In general, forensic sciences include a broad interdisciplinary group of applications of physical and biological sciences as well as various technologies applied in civil and criminal justice. Forensic sciences cover areas from psychology, pathology, psychiatry, toxicology, entomology, anthropology, and odontology up to pure forensic chemistry issues [1–3]. In particular, forensic analytical chemistry is a discipline that is applied to crime scene analysis and law [4]. Therefore, forensic chemical analysis involves qualitative and quantitative determinations of a wide range of analytes including DNA, drugs of abuse, weapons, explosives, paints, solvents, and fire accelerants, besides many other various materials at a crime scene [5–7]. On the other hand, forensic samples also include a wide range of matrices, e.g., biological tissues, biological fluids, water, soil, food, etc.

Growing concerns about growing crimes have generated a tremendous demand for developing more efficient analytical procedures. In addition to essential analytical characters, current forensic analysis research is focusing on developing modern analytical methods enjoying rapidity, inexpensiveness, sensitivity, safety for handling solutions, safety for the environment, and the possibility of on-site tests.

Flow injection (FI) techniques are presented as powerful tools, which enjoy unique features involving automation, miniaturization, versatility, and inexpensiveness. These features could not only meet the requirements of forensic analysis, but also could meet the requirements of almost all modern chemical analysis. Therefore, FI techniques have attracted great attention by many researchers owing to their ability to fulfill the current demands of chemical analysis.

A literature survey was carried out by the Scopus® database using the key words "flow injection," "sequential injection," "bead injection," and "lab-on-valve." These terms cover all generations and versions of FI techniques. The literature survey enumerated more than 10,000 articles published from 1975, the inception of FI techniques, to the beginning of 2010. Within the extracted results, a further sub-survey was conducted searching for various applications including pharmaceutical, environmental, food, biochemical, or clinical and forensic. The results obtained are depicted in Fig. 1. It has been found that pharmaceutical analysis has taken the lion's share, which could be attributed to the requirements of the pharmaceutical industry for auto-analysis and cost-effectiveness. The figure also shows that

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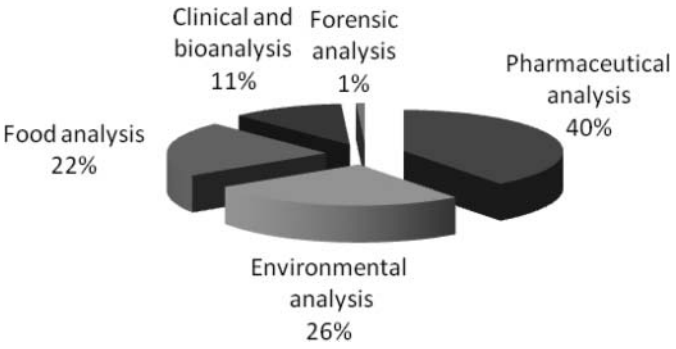

FIG. 1. Applications of FI techniques to various analytical fields.

FI techniques are overlooked in the field of forensic analysis since relatively few publications were reported.

The impetuses for writing this article are that the author has not found an article reviewing the applications of FI techniques to forensic chemical analysis and the inattention of forensic analytical chemists on the potential of FI techniques. This article comprehensively reviews the applications of FI techniques, including all generations and versions, to forensic analysis. Prior to the review, the article also provides a brief historical background on the developments of FI techniques while highlighting their remarkable advantages. Furthermore, future perspectives in the applications of FI techniques to forensic analysis are discussed.

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HISTORICAL BACKGROUND ON THE DEVELOPMENTS OF FLOW INJECTION TECHNIQUES

The need for technological innovations for the improvement of analytical procedures propels the search for new approaches and their efficient applications. Toward this end, FI techniques have been proposed as a strategy for automatically handling solutions and consequently for carrying out methods related to wet chemical analysis. During the previous four decades, FI techniques were being continuously developed, which resulted in an extended family including, currently, three generations and five versions.

Primarily, the inception of flow-based analysis was in the mid-1950s by introducing the segmented flow analysis (SFA) technique [8]. Due to its automation, SFA had been readily accepted by overloaded clinical laboratories for routine diagnostic purposes and, later, by environmental, agricultural, oceanographic, and industrial laboratories [9]. However, SFA suffers mainly from both the debubble processing of a fluid before entering a detector and the consumption of large volumes of reagents and samples.

In the mid-1970s, the first generation of the family of FI techniques, named flow injection analysis (FIA), was introduced by Ruzicka and Hansen [10]. A typical FIA manifold consists of a peristaltic pump (PP), two-position valve (TPV), reaction coil (RC), and detector. FIA is accomplished by injecting a plug of sample into a flowing carrier stream. Besides enjoying simplicity of configuration, ease of operation, and low cost, FIA has overcome the drawbacks of SFA. In 1990, Ruzicka and Marshall proposed sequential injection analysis (SIA), as the second generation, with dramatic modifications and developments [11]. A basic SIA manifold comprises a syringe pump (SP), holding coil (HC), MPV, RC, and detector. SIA enjoys significant advantages over FIA because the frontal applies a miniaturized fully-automated bi-directional discontinuous precisely-choreographed flow. The programmable flow of SIA offers also the use of widely different chemistries and renders analytical methods, especially kinetic ones, more accurate and precise. Moreover, the use of a MPV allows for conducting a convenient automated calibration. The third generation, i.e., bead injection analysis (BIA), was developed in 1993 by Ruzicka *et al.* [12]. BIA is the combination of the use of beads with a flowing stream of a solution into a FIA or SIA system. That combination provides special applications, which are frequently dedicated to bioanalysis.

For more development, some versions of FI techniques have also been proposed. In 1994, Reis *et al.* introduced MCFIA to solve the main problem of FIA, i.e., the continuous flow [13]. Multi-commutation FIA is based on the use of several independent automatically controlled solenoid micro-pumps. In 1999, Cerda *et al*. designed multi-syringe FIA [14], which comprises many SPs. MSFIA gathers, in the same methodology, all the advantages of the parent FIA, SIA, and MCFIA. In 2000, Ruzicka introduced a more miniaturized SIA version that is termed microSIA-lab-on-valve, which allows for more downscaling reagent and sample volumes [15]. With the exception of an integrated micro-conduit system that is a transparent monolithic structure, those peripherals used in SIA are also used in μSIA-LOV. In another development, the exploitation of pulsed flows led Lapa *et al*. to propose multi-pumping FIA in 2002 [16]. A MPFIA manifold involves several pumps achieving such tasks as driving solution, improving mixing conditions, introducing reagent and samples into the analytical path, establishing tandem streams, stopping the sample, and providing commuting facilities.

Although extensive developments have been dedicated to the FI techniques, they had suffered from the limitation of separation and multi-component determination. In 2003, Satinsky *et al*. proposed sequential injection chromatography (SIC) to overcome that limitation [17]. SIC is basically built on a typical SIA manifold by installing a short monolithic column (10–50 mm) allowing for efficient separation. Recently, a high pressure SP and MPV were installed in SIC to accelerate separation and reduce back-pressure. In general, a recent manuscript describing in more detail the principles and development of FI techniques was published by the author [18].

POTENTIALS OF FLOW INJECTION TECHNIQUES

In spite of their variations in instrumentation and methodologies, most of FI techniques, if not all, gather outstanding

features including automation, miniaturization, versatility, simplicity, and inexpensiveness. Those features offer valuable benefits for forensic analysis.

Automation provides safety for handling forensic samples and related reagents, which are most probably hazardous. Automation also allows for conducting one-shot on-line analytical procedures including sample treatment, developing reaction, separation, and measurement. Furthermore, accuracy and precision are significantly enhanced by automation. Additionally, effort and manpower are drastically minimized by automation.

On the other side, in many forensic cases, the ability to perform a point-of-collection analysis can play a pivotal role in inquiry requirements. Toward this end, the miniaturization of FI techniques allows for conducting on-site tests. Moreover, miniaturization reduces the consumption of reagents and samples and thus provides better safety for the environment. Furthermore, miniaturization and automation work together to provide a high sample throughput.

Forensic science is typically a field that involves the interface between different analytical technologies. In this issue, due to their versatility, FI techniques look particularly promising. Various analytical devices, detectors, and analytical instruments could be successfully hyphenated with FI techniques. Moreover, versatility and automation work hand in hand to provide more efficient on-line analytical procedures. More details on the potentials of FI techniques were recently discussed by the author elsewhere [18].

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APPLICATIONS OF FI TECHNIQUES TO FORENSIC CHEMICAL ANALYSIS

Background

Based on the literature survey as illustrated in Section 1, it has been found that FI techniques have received less attention in the field of forensic analysis. However, various applications were reported in that field including the assay of DNA, drugs of abuse, toxicologically relevant chemicals, weapons, and explosives, as well as post-mortem estimation. In more detail, it has been found that DNA analysis has received more attention than other fields of forensic analysis.

Because DNA analysis is applied for purposes other than forensic, additional literature survey was conducted to widen this topic. The key words DNA, flow injection, sequential injection, bead injection, and lab-on-valve were included in that survey while the key word forensic analysis was excluded. The following sections describe a comprehensive review of the applications of FI techniques to forensic analysis.

Applications to DNA Analysis

Research on developing DNA analytical methodologies always looks for minimizing cross-contamination, reducing volumes of reagents and samples, as well as achieving better sensitivity, selectivity, and rapidity. The possibility of coupling FI techniques with various detection approaches gained satisfactory selectivity and sensitivity of ultra trace levels of DNA in various matrices. Because of their high sensitivity and selectivity, chemiluminescence and fluorescence detectors have received special attention. In the literature, it has been found that the range of limit of detection of DNA obtained by chemiluminescence was 7.5×10^{-4}–0.2 ng-mL [19–26] while that obtained by fluorescence was 0.1–70.0 ng-mL [26–31]. In those applications, various chemical systems were employed for chemiluminescence enhancement including rhodamine B-Ce(IV) [22–24], Luminol-H_2O_2 [22], Cu^{2+}-H_2O_2 [23], and enzymeatically produced H_2O_2 [24]. On the other hand, other chemical systems including 9,10-anthraquinone-2,6-disulphonic acid-ethanol [25] and Ce(IV)-Na_2SO_3-Tb(III)-fluoroquinolone antibiotic [26] were used for chemiluminescence quenching. Moreover, the chemical systems of Hoechst 33258 [27], ethidium bromide [28], berberin [29], and picogreen [30] were used for fluorescence enhancement while 3,3′,5,5′-tetramethylbenzidine dihydrochloride was used for fluorescence quenching [31].

On the other hand, FI techniques with visible [32] and UV spectrophotometry [33] were also utilized for DNA assay. In the best cases, the LODs obtained in those methods did not go below 70 ng-mL.

Electrochemical detection, namely ameprometric and voltametric [34–36], was also used with FI techniques for DNA analysis. In those methods, different electrodes were developed, including peroxidase-mercaptopropionic acid-modified gold [34], polypyrrole-coated [35], and tris(2,2′-bypridyl)dichlororuthenium(II) modified carbon [36]. In general, the LOD using ameprometric detection (>0.5 μg-mL) was better than that using voltametric detection (>500 μg-mL).

In another method, a couple of FIA with mass spectrometry was used for DNA assay [37]. The FIA manifold was utilized for on-line desalting to eliminate interference from sodium, potassium, and magnesium ions.

Recently, a FIA capacitive biosensor system was developed to detect a trace amount of DNA [38]. The method was based on the affinity binding between immobilized histone and DNA. Histones were immobilized on gold electrodes covered with self-assembled monolyer of thioctic acid. The method achieved acceptable LOD (0.01 ng-mL) and a wide linear range (0.01–10 ng-mL). In a more recent work, FIA with chemiluminescence was used for the detection of DNA hybridization and single-nucleotide polymorphisms [39]. A signal amplification strategy based on bio-bar-code functionalized magnetic nanoparticles as labels holds promises to improve the sensitivity and detection limit.

It is worth noting that a valuable benefit of exploiting FI techniques for DNA analysis, in general, is the high sample frequency, which recorded a range of 24–112 sample/h. Among all generations and versions of FI techniques, μSIA-LOV has proved more efficient procedures due to its more down-scaling solution volumes. Figure 2 shows a schematic diagram of a typical μSIA-LOV manifold constructed for DNA assay.

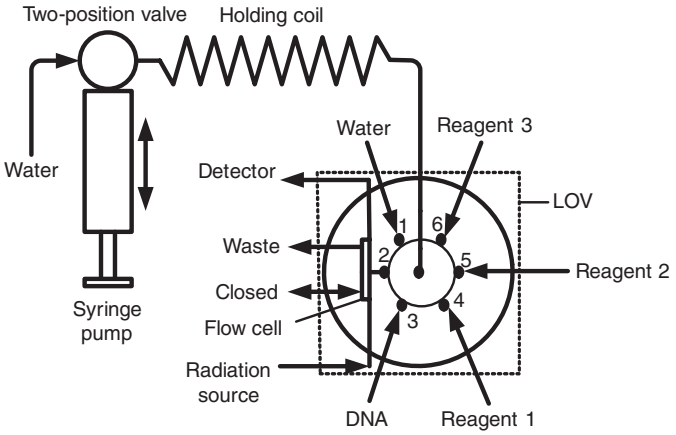

FIG. 2. A schematic diagram of a typical μSIA-LOV manifold utilized for DNA assay.

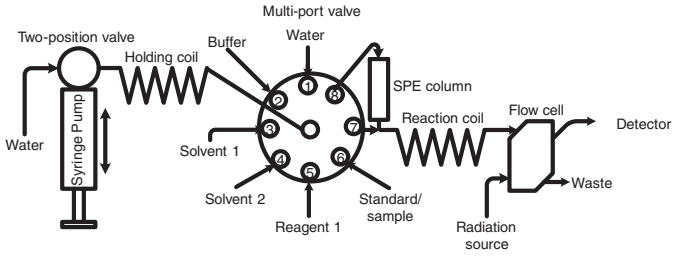

FIG. 3. A schematic diagram of a SIA manifold constructed for on-line solid-phase extraction (SPE), developing reaction and spectrophotometric measurement of some drugs of abuse in urine samples.

Applications to Drugs of Abuse Analysis

The illegal use of many narcotic drugs has created the need to detect these substances in any suspected materials and to identify and/or quantify the parent compounds and their metabolites in biological fluids and hair samples. Most official procedures recommended for the analysis of drugs of abuse are based on gas chromatography-MS. Due to the accelerating mis-use of narcotic drugs, researchers developed many alternative methods based on such techniques as high performance liquid chromatography or capillary electrophoresis with UV-absorbance, fluorescence, electrochemical, or MS. Additionally, FI techniques have been approved as successful applications. Unfortunately, most of the FI methods for drugs of abuse analysis did not discuss their applicability to forensic purposes. In 2008, Francisa *et al*. reviewed the chemiluminescence detection of opium poppy (*Papaver somniferum*) alkaloids in many matrices for various purposes [40]. The following section reviews the applications of FI techniques to drugs of abuse analysis for only forensic purposes from 1975 to the present.

FIA [41–44] and SIA [45] with chemiluminescence detection were utilized for the quantification of morphine [41, 42, 44, 45] and heroin [43]. Acidic permanganate was used for all methods while different enhancers were used including tetraphosphoric acid [41], sulfite with ploypHosphoric acid [42], polyphosphate [43], and hexametaphosphate [44, 45]. The proposed FIA [41–44] and SIA [45] methods were applied to urine [42], aqueous process streams [41, 44], non-aqueous process streams [45], and drug seizure samples. The LOD obtained in those methods ranged from 7×10^{-9} to 1×10^{-6} mol-L. In another works, tris (2,2-bipyridyl)ruthenium(II) was used with FIA to assay codeine [46, 47] and heroin [43] in industrial process samples [46], heroin seizures, and drugs seized from illegal suppliers [47]. Papaverine in biological fluids was also determined using a FIA technique [48]. Papaverine was reacted with cerium(IV) and sulfite to produce chemiluminescence. The LOD obtained was 9×10^{-8} mol-L. In general, chemiluminescence detection used in those methods exhibited remarkable sensitivity and complementary selectivity for drugs of abuse in samples with complex matrices.

Recently, Idris' research group constructed SIA manifolds (Fig. 3) suitable for automating on-line procedures for the assay of trifluperazine [49] and morphine [50] in human urine. The on-line procedures included sample treatment, developing reaction, and spectrophotometric measurement. For sample treatment, a SIA-solid-phase extraction process was conducted in order to perform sample clean-up, pre-concentration, and extraction. The SIA-SPE process was conducted in a homemade microcolumn that was installed in a SIA manifold (Fig. 3). The developing reaction for trifluperazine assay was the oxidation of the drug by cerium(IV) in sulfuric acid media. The reaction produced a free radical species of trifluperazine, which was spectrophotometrically detected at 500 nm. The developing reaction for morphine assay was the couple of the drug with the diazonium salt of aniline hydrochloride. The reaction produced an azo-morphine derivative, which was spectrophotometrically detected at 390 nm. In both SIA methods, satisfactory LODs (18.2 and 23 ng-mL for trifluperazine and morphine, respectively) were obtained. The sensitivity of those methods was improved by three approaches, i.e., pre-concentration, optimizing the developing reactions, and the use of an extended pathlength (50 mm) of a flow-cell. The full-automation of the on-line analytical procedures rendered the methods rapid (sample frequency 11 sample-h). The full-automation also potentially improved the precision of the both methods in the terms of repeatability (relative standard deviation $< 3.9\%$) and intermediate-precision (RSD $< 4.3\%$).

Idris' research group also developed another SIA-SPE procedure for a total of 19 drugs of abuse, including alkaline, neutral, and acidic, in human urine [51]. The treated samples were, then, subjected to separation and quantitative determination using CE with UV detection. In that method, satisfactory LODs (5–30 ng-mL) were also obtained. The sensitivity was enhanced by both pre-concentration, which was obtained by SIA-SPE, and sample stacking that was performed in a CE system.

In general, a literature survey was conducted on the application of FI techniques to SPE for various analytes in a wide range of sample matrices. In this topic, it has been found that most of

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SPE procedures utilized FIA while few SPE procedures utilized SIA. However, SIA has proved a more convenient tool for SPE processes, which could be attributed to its full-automation and more miniaturization as well as the use of MPV.

Overall, FI analytical procedures for quantification of drugs of abuse offered safety for handling samples and reagents, which are highly hazardous. Another valuable benefit is that the potential reduction of reagents, which are usually expensive and highly controlled.

Applications to Analysis of Other Toxicologically Relevant Substances

A FIA system was exploited to introduce dissolved samples into MS [52]. In that work, 22 casework samples were collected during autopsies by the police or found with patients at hospital. Samples were collected from mouth, esophagus, gastric contents, and illegal seized drugs. The aim of the work was to identify the toxicologically relevant compounds sildenafil, dihydrocodeine, diphenhydramine, oxprenolol, N-methyl-3,4-methylenedioxyamphetamine, morphine, amphetamine, caffeine, pemoline, orphenadrine, m-chlorphenylpiperazine, and tramadol. In another work, FIA was also used to introduce plasma samples into MS for determination of arsenate [53]. After washing plasma with trichloroethylene (TCE), arsenate in the aqueous layer was reacted with pyrrolidinedithiocarbamate (PDC, $C_4H_8NCSS^-$). The produced $As(PDC)_3$ was extracted with methyl isobutyl ketone (MIBK). A 1-μL aliquot of the MIBK layer containing $As(PDC)_3$ was introduced into the MS in the direct FIA mode.

In general, FIA has proven itself as an efficient tool for rapid sample introduction into MS. Since FIA is not limited by separation run times, it has real speed advantages. FIA provides the greatest ease of automation and use for large numbers of samples. However, a major drawback to FI-MS is ion suppression due to coeluting sample components. Thus, the approach is more desirable in qualitative analysis [54].

Applications to Weapon and Explosive Analyses

The literature survey has enumerated few publications reporting applications of FI techniques to weapon and explosive analyses. In a previous method, a FIA system with amperometric detection was constructed for determining lead azide [55]. It should be noted here that there is a requirement for lead azide, as a primary explosive, to be determined by the measurement of azide in order to avoid mis-leading results from other forms of lead. In that method, the analyte was oxidized at a glassy carbon electrode. Favorable sensitivity with LOD of 50 ng-mL in soil samples was obtained.

Another FIA system with potentiometric detection was developed for determining trans-dichloro(2-chlorovinyl)arsine (Lewisite) in ambient air in near real time [56]. Lewisite monitoring in air is required to support arms control treaty inspections, weapons destruction processes, and remediation of hazardous waste sites. In that method, the FIA system was used to integrate a gas permeation membrane sampling unit to a detector, which was based on the constant-current mode of potentiometric stripping analysis. The method indirectly measured Lewisite in ambient air by collecting vapor-phase Lewisite across a thin-walled rubber membrane. Thereafter, Lewisite was hydrolyzed to form arsenite ion for potentiometric detection.

In another work, Lancaster's research group reported the construction of a SIA system for conducting an on-site screening assay method for the degradation products of chemical weapons during challenge inspections [57]. The same research group also reported a more specific work on the use of a SIA system with colorimetric detection for quantitatively determining the final degradation product of phosphoric acid based chemical warfare agents [58]. The method involved a chromogenic reaction of the analyte with molybdenum blue. An acceptable LOD (50 ng-g in soil samples was obtained.

In the same topic, FIA was also used for prior analysis, for cleaning lead bullet samples [59]. Samples were then subjected to further analysis for the determination of some trace elements using inductively coupled plasma-MS [57]. Additionally, another FIA system was exploited for injecting solutions into a microchip system for the separation and determination of some nitroaromatic explosives and organophosphate nerve agents [60].

SIA was also applied for the quantitative determination of 2,4,6-trinitrotoluene (TNT) [61]. The method was based on the derivatization reaction of TNT with sodium sulfite in a basic acetone medium. The method was precise enough (RSD 6.1%), sensitive (LOD 80 μg-g for 300-mg soil samples), and rapid (20 sample/h). The method also proposed an on-line SPE procedure using SIA for pre-concentration of TNT in water samples.

In general, articles reporting the utilization of FI techniques for weapon and explosive analyses highlighted mainly the benefits of the possibility of conducting on-site tests, rapid response, high reproducibility, high sensitivity, and minimal waste production.

Application to Post-mortem Estimation

The estimation of the time since death, which is known as post-mortem interval, is a main issue in the field of forensic science and legal medicine. In this issue, a recent publication reported the construction of a unique SIA manifold (Fig. 4), which was utilized for the potentiometric determination of potassium [62]. In the same procedure, hypoxanthine in vitreous humor was also determined using spectrophotometric detection [62]. The levels of hypoxanthine and potassium are good indicators for the estimation of post-mortem interval. The vitreous humor was regarded as the ideal extra-cellular fluid for determining the concentrations of hypoxanthine and potassium. As depicted in Fig. 4, the SIA manifold comprises a PP, solenoid valve, MPV, activated glass beads-uricase reactor, activated glass beads-hypoxanthine reactor, activated glass beads-reactor, electrochemical cell, and spectrophotometer. By measuring both parameters hypoxanthine and potassium, the accuracy of the

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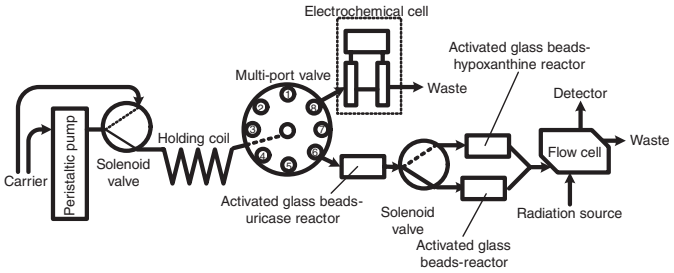

FIG. 4. A schematic diagram constructed for simultaneous potentiometric determination of potassium and spectrophotometric determination of hypoxanthine in vitreous humor.

estimation of post-mortem interval was increased. Moreover, the effect of factors influencing values in post-mortem chemistry was minimized. The automation and miniaturization of SIA rendered the proposed procedure repeatable (RSD $< 5\%$), rapid (sample frequency 30 sample/h), and safe for the environment (chemical waste 2.7 mL/sample).

CONCLUSIONS AND FUTURE PERSPECTIVES

From the current review article, the following conclusions and future perspectives can be made:

- The potentials of FI techniques could practically provide endless possibilities for automating and miniaturizing reagent and sample handling and consequently carrying out procedures dedicated to forensic analysis as initial tests. More importantlly, SIC, namely, could offer the possibility of conducting confirmational forensic tests when selective and sensitive detectors such as MS are used.
- The automation of FI techniques offers high-secure reagent and sample handling and high sample throughput. Automation also allows for developing one-shot on-line analytical methodologies. Furthermore, accuracy and precision could be significantly enhanced by automating analytical procedures utilizing FI techniques.
- The miniaturization of FI techniques reduces the consumption of forensic samples and related reagents and thus minimizes waste production. Miniaturization also works hand in hand with automation to provide more rapid analysis.
- Due to their versatility, FI techniques can be hyphenated with various detectors allowing for conducting selective and sensitive forensic analytical methods for various analytes in various matrices.
- Due to its downscaling, μSIA-LOV, especially, is highly recommended for forensic assays involving rare samples and/or expensive reagents.
- SIC, as a recently introduced technique, is promising for forensic analysis involving multi-component determination with separation procedures.

Eventually, it is hoped that this review article attractively demonstrates the potentials of FI techniques and addresses useful applications to forensic analysis. It is also hoped that the article arouses the interest of forensic analytical chemists in the potentials of FI techniques.

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ABBREVIATIONS

BIA	bead injection analysis
CE	capillary electrophoresis
FI	flow injection
FIA	flow injection analysis
HPLC	high performance liquid chromatography
HC	holding coil
ICP	inductively coupled plasma
LOD	limit of detection
MS	mass spectrometer
μSIA-LOV	micro-sequential injection analysis-laboratory-on-valve
MCFIA	multi-commutation flow injection analysis
MPV	multi-position valve
MPFIA	multi-pumping flow injection analysis
MSFIA	multi-syringe flow injection analysis
PP	peristaltic pump
RC	reaction coil
RSD	relative standard deviation
SFA	segmented flow analysis
SIA	sequential injection analysis
SIC	sequential injection chromatography
SPE	solid-phase extraction
SP	syringe pump
TPV	two-position valve

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