Recent developments in flow-analysis vibrational spectroscopy

S. Armenta, S. Garrigues, M. de la Guardia

This review deals with developments in the new century on the use of vibrational spectroscopy techniques for detection in flow-injection analysis (FIA) systems. To provide a picture of the evolution, highlights and future developments in this field, we revisited Fourier transform infrared (FTIR), in the mid-IR and near-IR ranges, and FT-Raman spectrometry applications using different approaches, from classical FIA to modern (sequential injection analysis (SIA) or multicommutation). We used the analytical abstracts database for 2000–06 for the literature search, but we based this review very much on the experience of our team in this field.

Keywords: FIA; Flow-injection analysis; Fourier transform infrared; FTIR; Multicommutation; Raman spectrometry; Sequential injection analysis; SIA; Vibrational spectroscopy

S. Armenta, S. Garrigues*,
M. de la Guardia
Department of Analytical Chemistry,
Universitat de València,
Edifici Jeroni Muñoz,
50[th] Dr. Moliner 46100
Burjassot, Valencia, Spain

1. Introduction

Flow systems are commonly used to solve a large variety of analytical problems from different fields, including environmental, biochemical and process analysis. The concept of flow-injection analysis (FIA) was introduced in the mid-1970s by Ruzicka and Hansen [1]. The interest in FIA techniques as an exceptionally effective means of mechanizing various procedures of wet chemical analysis has been exponentially increasing in the laboratory because of the advantages offered in automated sample processing, high repeatability, adaptability to microminiaturization, containment of chemicals, waste reduction, and reagent economy in systems that operate at microliter levels. The possibility of using FIA with a whole arsenal of detection methods of modern analytical chemistry has proved to be of great interest to analytical researchers.

The fast, intensive development of FIA methodology has been due to several factors essential for routine analytical determinations (e.g., limited sample consumption, short analysis time based on transient signal measurements in flow-through detection, and possibilities of carrying out on-line separation, preconcentration or physicochemical conversion of analytes into detectable species). Detection is most frequently made in the ultraviolet/visible (UV/Vis) range for both molecular and atomic analysis. However, in life sciences, different luminescence techniques are gaining popularity. Electrochemical techniques (e.g., amperometry and potentiometry) have gained new life by coupling them to flow-based sample-handling techniques.

Vibrational spectroscopy is of special interest as a detection technique in flow systems because of the molecule-specific information contained in infrared (IR) and Raman spectra, and, for this reason, the FIA philosophy has been incorporated in some commercially-available analyzers based on mid-IR (MIR) and near-IR (NIR) transmission measurements (e.g., Milkoscan, Dairy Milk Analyzer, Bentley 150 and Bentley 2000 analyzers, Winescan, Petroscan or CSP-IR).

The advantages offered by IR and Raman for FIA detection are:

(i) fast monitoring of the whole spectrum;
(ii) high resolution and wide wavenumber range;
(iii) many bands that can be employed for determination of each single compound;
(iv) simultaneous control of several compounds in the same sample;
(v) the possibility of eliminating band overlap by using simple strategies (e.g., derivative spectrometry or modeling the whole signal by multivariate calibration) [2].

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*Corresponding author.
Tel.: +34 963 543 158;
Fax: +34 963 544 838;
E-mail:
salvador.garrigues@uv.es

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Although sensitivity limitations reduce the use of molecule-specific information available in vibrational spectra to the analysis of main and minor components, the use of new detectors and the combination of solid-phase extraction (SPE) and FIA can be useful for trace analysis.

In spite of the above advantages and the fact that flow-analysis-vibrational spectrometry is a mature discipline, the applications available are far below the level that it merits.

This review is devoted to presenting the state-of-the-art and the scope of on-line vibration-based detection strategies. We present some studies that have fundamentally contributed to the development and the evolution of flow-analysis-vibration-based techniques and the main fields of its practical applications.

2. Classical FIA

The first generation of FIA techniques, now called classical FIA, is also probably the most widely utilized. In its simplest form, the sample zone is merged or injected into a flowing carrier stream of reagent. The sample solution disperses into the reagent and is recorded by an appropriate detector.

A typical FIA manifold comprises pump, injection valve, detector, and tubing manifold (Fig. 1). This manifold is very simple, and innovative research has integrated a wide range of different sample-processing steps into FIA methodologies. These include dilution, pre-concentration, solvent extraction, gas permeation and reactions with immobilized reagents.

The main reasons for the success of FIA over conventional manual techniques are:
(i) reduced labor costs due to automation;
(ii) great precision due to the assays being performed mechanically;
(iii) high sample throughput to the assays being performed mechanically; and,
(iv) consumption of small amounts of sample and reagent, and generation of a small amount of waste due to the small scale of the assays.

2.1. Mid-IR

The synergistic combination between FIA and Fourier transform IR (FTIR), developed in the past 15 years, provides:
(i) a simple, fast and reproducible way for loading IR flow cells (transmittance or attenuated total reflectance (ATR));
(ii) enhanced repeatability and accuracy because of the lack of sample handling; and,
(iii) significant reductions in reagent consumption and time of analysis [2].

In addition, the major merits of IR detection in flow-analysis systems include:
(i) an easy way of operating;
(ii) real-time detection;
(iii) low maintenance; and,
(iv) possibilities of multicomponent analysis.

Usually, FIA–FTIR has been applied for single-component analysis, but multi-component analysis can also be carried out. The absence of a separation step does not preclude identification and quantification of several analytes in a same sample. For example, introduction of multivariate regression methods has enabled simultaneous quantification of several compounds, even in cases of strong band overlap.

Commercially-available applications have been the basis of a series of trademarked analyzers available in the market (e.g., Milkoscan (FOSS), Dairy Milk Analyzer (Astori S.N.C.) or Bentley 150 and 2000 (Bentley Instruments) are typical examples that can determine fat, proteins, dry matter, non-fat solids, lactose and energy values in dairy-milk products with a sampling frequency of 150–450 samples/hour, based on mid-IR transmission spectra).

The Winescan (FOSS), which allows determination of the major quality parameters of wine and grapes, and the CSP-IR analyser from ChromaSpec are useful for determination of different properties and physical parameters of gasoline, diesel, lubricating oils and refinery fractions from their IR spectra measured on untreated samples.

Since Curran and Collier made the first study focused on the analysis of synthetic samples in 1988 [3], in which phenyl isocyanate was analyzed using a dispersive IR spectrometer by transmittance measurements, the FIA–FTIR technique has been successively applied to the determination of diverse analytes in several matrices, using different flow-through cells and FI approaches, as can be seen in Table 1.

Our research group has analyzed different pesticides using FIA–FTIR measurements, obtaining precision values of the order of 0.18–8% and acceptable values for the limit of detection (LOD) for their determination in pesticide formulations.

Regarding other applications of the methodologies developed for FIA–FTIR using transmittance measurements, we must highlight the determination of different analytes (e.g., phosphate, ethanol and CO_2) in food matrices. Representative examples of this approach are those where a sample is mixed with a reagent and different quality parameters of oil monitored (peroxide value [10] and free fatty acid content [11]) by means of FIA–FTIR. The determination of phosphate in soft-drink samples used a Fabry-Perot quantum-cascade laser (QCL) as a powerful light source for MIR detection in FIA [15] (see Fig. 1A). The use of QCL instead of an interferometer results in real-time spectral data