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Editorial

Yesterday, Today and Tomorrow of Supercritical Fluid Extraction and Chromatography

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ABSTRACT

The aim of this special issue of the American Journal of Analytical Chemistry (AJAC) on Supercritical Fluids is to promote knowledge about this rapidly developing area of analytical chemistry, which is very useful in fields such as the pharmaceutical and pesticide manufacturing industries, food production, clinical medicine and environmental studies. In this issue, the use of Supercritical Fluids (SFs) in Supercritical Fluid Extraction (SFE) and Supercritical Fluid Chromatography (SFC) is described.

Keywords: Supercritical Fluids; Supercritical Fluid Extraction; Supercritical Fluid Chromatography

SFE is used for analytical, semi-preparative and industrial-scale processes. Despite similarities in the SFE and SFC processes, the instrumentation is very different. In SFC, there are two different instrumental approaches: Capillary Column Supercritical Fluid Chromatography (CCSFC) and Packed Column Supercritical Fluid Chromatogramphy (PCSFC). The CCSFC instrument resembles a gas chromatograph, although it differs in many respects. PCSFC has many features of High-Performance Liquid Chromatography (HPLC). As mentioned by I. Brondz in [1], in chromatography, the SFC occupies a position somewhere between Gas Chromatography (GC) and High-Performance Liquid Chromatography (HPLC).

Critical phenomena were discovered by Baron Charles Cagniard de la Tour (1777-1859) 190 years ago, in 1822 [2,3]. First described as an exotic curiosity, later developed into highly advanced analytical and industrial technologies. In 1869, T. Andrews (1813-1885), who worked with gas liquefaction, undertook a systematic study of CO_2 at the gas—liquid critical point, the results of which are presented in [4]. The enhancement of solubility of different substances in SFs was described by J. B. Hannay and J. Hogarth in 1879 [5], and later in [6]. Further study was undertaken by J. B. Hannay [7]. It was only much later that the useful observations were translated into analytical and industrial processes.

The first attempt to utilize the phenomenon in industry was patented by K. Zosel [8].

As early as 1958, J. Lovelock expressed the idea of using SFs in chromatography [9]. This has subsequently been described by many authors. The first practical use of SF in chromatography was demonstrated by E. Klesper *et al.* [10]; they designed the first working model of a chromatographic instrument using SF as early as 1961. S. T. Sie and G. W. A. Rijnders were possibly the first to introduce the terminology “chromatography with supercritical fluids” or “supercritical fluid chromatography” [11].

The patent that was registered by Zosel [8] practically established the basis for SFE in industrial processes. This was the starting point for a steadily growing number of patent applications in the field of SFE processing, both in research and in industry. Today, for example, decaffeination of harvested coffee beans is almost exclusively carried out using SFE, mainly with CO_2 as supercritical fluid. SFE is also applied to processing hops and spices, and producing pungents and flavors from many natural products.

However, in contrast to SFE until the mid-1980s, SFC was not well received in research circles, mainly because of the unavailability of commercially available analytical instruments and the unprofessional approach of some researches toward experimental basics, and attempts to adopt the GC or HPLC principles to SFC. A good example is the vain attempts to develop the technique and instrumentation in the Laboratory of Assistant Professor Tyge

Greibrokk at Analytical Chemistry, Department of Chemistry, University of Oslo, Norway, between 1980 and 1985. The "great success" of these attempts resulted in the University of Oslo, Mathematics and Natural Sciences Faculty's decision to stop all experiments involving the use of SFC; subsidies were cut and there was to be no future financing of these experiments.

It was then that I decided to commence with SFC experiments in the Laboratory of Analytical Chemistry Department of Chemistry, University of Oslo, Norway, although there I only found an old, disintegrated CCSFC and encountered resistance from staff when attempting to use it. I subsequently got away from the Department of Chemistry to the Department of Biochemistry, and then used my private funds to buy the instrumentation I required to conduct experiments. Alarm bells from the Department of Chemistry reached the Department of Biochemistry, creating a tense atmosphere. Successful important publications describing new developments in SFC-MS and SFC with multi-detection technique approach were nonetheless published [12-15]. However, it became necessary to leave the Department of Biochemistry at Oslo University, and continue working on this field at a new location, the Norwegian University of Life Sciences, Department of Chemistry, Biotechnology and Food Sciences, Ås, Norway. A series of successful experiments using SFC-MS was carried out, as described in [13-19]. Several other studies were undertaken, two of which are described in this special issue.

To date, the question of the usefulness of SFC has not been adequately answered. This is mainly because two quite different techniques (CCSFC and PCSFC) are combined. Furthermore, marketing the instrumentation for use for solving unsuitable tasks may be inaccurate.

As CCSFC resembles GC, nearly all detectors used for GC can be utilized for CCSFC. There is no restriction on the utilization of GC capillary columns in CCSFC. The current availability and selection of specially manufactured capillary columns for CCSFC is, however, poor. Generally, the use of dry CO_2, without co-solvents and modifiers, is standard. In programmable CCSFC processes, the amounts of co-solvent and modifier are difficult to determine.

In PCSFC, all detectors usually used for HPLC may be used, but the detectors should be suitable for use at high pressure. There are some exceptions to this. A MS, or a corona charged aerosol detector, connected to a PCSFC as it is described in [14,15]. Because of the nature of SFC, it is possible to gather extensive information about the molecular structure of a substance under an eluted peak by using a multi-detector approach [14,15]. Connecting to the PCSFC a series of detectors, such as UV-Vis-DAD, MS and a corona charged aerosol detector enables a scientist to detect the presence of different chemical compounds under the eluted peaks, and then construct a useful fingerprint, for comparing different systems and organisms [15]. In contrast to CCSFC, PCSFC can be programmed in terms of time, and concentrations of co-solvents and modifiers. Hence, a broad range of solvent strengths can be created. This means that PCSFC can be used for a wide variety of substances. Both CCSFC and PCSFC operate at low temperature, about 35˚C, which is an advantage for thermo-liable molecules. In most systems, the eluent does not contain water. Hydrolysable molecules can be analyzed and separated.

It is only over the past decade that columns especially manufactured for PCSFC have appeared on the market; earlier, the use of HPLC columns for PCSFC was common. Even today, however, the choice of specially manufactured PCSFC columns is poor.

The advantages of PCSFC, compared with other chromatographic techniques such as GC and HPLC, is the good resolution of chiral molecules and low temperature of operation. However, progress in this field has been hampered by the unavailability of columns suitable for the simultaneous high resolution of enantiomers and isomers. Chiral columns usually have excellent ability to resolve enantiomers in relatively simple mixtures; however, than it should be resolved complex mixtures of enantiomers with isomers the existing chiral columns have wick ability to perform this. A common challenge in the separation of enantiomers is in cases where the peak of one of the enantiomers is hiding another substance in the form of an isomer, as it described in [20,21].

The unique ability of SFC to resolve enantiomers has not been fully exploited yet. The production of high purity enantiomers from complex mixtures is a future area for analytical, semi-preparative and industrial PCSFC. Resolution and separation of enantiomers in pure state from complex mixtures is described in the present AJAC special issue on Supercritical Fluids by I. Brondz and A. Brondz [22].

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