



## Review

# Gas chromatography on wall-coated open-tubular columns with ionic liquid stationary phases



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## ABSTRACT

Ionic liquids have moved from novel to practical stationary phases for gas chromatography with an increasing portfolio of applications. Ionic liquids complement conventional stationary phases because of a combination of thermophysical and solvation properties that only exist for ionic solvents. Their high thermal stability and low vapor pressure makes them suitable as polar stationary phases for separations requiring high temperatures. Ionic liquids are good solvents and can be used to expand the chemical space for separations. They are the only stationary phases with significant hydrogen-bond acidity in common use; they extend the hydrogen-bond basicity of conventional stationary phases; they are as dipolar/polarizable as the most polar conventional stationary phases; and some ionic liquids are significantly less cohesive than conventional polar stationary phases. Problems in column coating techniques and related low column performance, column activity, and stationary phase reactivity require further exploration as the reasons for these features are poorly understood at present.

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## 1. Introduction

To appreciate the role ionic liquids might, or do, play in gas chromatography it is useful to begin with a brief summary of some of the milestones in the evolution of column technology. The early days of gas chromatography relied upon packed column technology and included the first use of ionic liquids as stationary phases [1–4]. The picture today is quite different, with wall-coated open-tubular (WCOT) columns (or capillary columns) occupying a dominant position. This is on account of the significant increase in separation performance and lower activity they afford. From a theoretical perspective, Golay demonstrated in 1957 that WCOT columns are capable of realizing a hundred-fold or higher increase in efficiency compared with a packed column, yet it was another quarter century before this was realized in practice [5]. Progress remained stalled until 1965 when Desty described a simple apparatus for drawing long lengths of capillary glass tubing from tube stock of standard dimensions [6]. The ready availability of glass capillary columns provided the catalyst that was needed for the theoretical and practical studies necessary to realize the preparation of columns with stable stationary phase films.

To facilitate wetting of the glass surface by the stationary phase a range of chemical and physical surface treatment procedures were developed and optimized [7–10]. Spreading of the stationary phase on the glass surface requires the surface tension of the stationary phase to be less than the critical surface tension of the glass. The surface energy of a smooth glass surface can be increased by altering its morphology by “roughening”. Roughening techniques include “particle-layer deposition” or “chemical bonding” of a thin intermediate organic film on the surface. In addition, roughening techniques are commonly used together with a number of surface conditioning treatments to control the concentration of metal ions and surface silanol groups. These techniques facilitated film formation but often at the expense of increased adsorption and catalytic activity [7]. To counter these undesirable effects a series of deactivation methods that allowed columns to be prepared with relatively inert surfaces essential for the separation of polar compounds were developed. Column preparation evolved as a multistep procedure increasing the complexity of the overall process.

In parallel to the development of surface modification procedures stationary phases evolved away from materials suitable for packed columns into analogous phases optimized for the more demanding conditions encountered with glass capillary columns [11–13]. All liquid films on curved surfaces are unstable and exhibit a natural tendency to decrease the interfacial energy at the gas–liquid interface leading to droplet formation (Rayleigh instability) [14]. This tendency is more pronounced as the temperature is varied. To mitigate this problem stationary phases of higher viscosity and/or capable of bonding to surface silanol groups, or containing substituents suitable for crosslinking, were developed. After more than a quarter of a century of effort glass columns with stable films had been developed with many of the pioneers associated with this effort recognized as the famous names in the field of gas chromatography.

However, a problem persisted. Glass columns were too fragile and required considerable skill in their daily use. The transfer of WCOT columns from the research laboratory to less specialized analytical laboratories had made little progress. Glass columns were widely regarded as unsuitable for use in an environment without dedicated experts to supervise every aspect of their use. This changed almost immediately with the introduction of polymer-clad fused-silica capillary columns by Dandeneau and Zerener [15]. The strength, flexibility, relative inertness, and the inherent straightness of column ends recommend fused silica as the column material of choice for column preparation. Earlier developments in stationary phase chemistry and an understanding of the role

column surface properties play in stable film formation allowed rapid development of fused-silica capillary columns. In a few years they were commodity items and quickly dominated commercial markets.

By the 1990s academic interest in column development was almost gone and complacency had set in. Developments did not stop completely but were increasingly incremental and occurred in the commercial sector with minimal transfer of this knowledge to their customer base. One exception was the development of the sol–gel process as a single step column preparation procedure as an alternative to the multi-step procedures commonly used by column manufacturers [16]. Column manufacturers improved the thermal stability of stationary phases and the inertness of column surfaces. Copolymers with stiffened backbones, such as silarylene–siloxane copolymers [17] and polar surface deactivating reagents [18] were two important developments of this type. As a marketing tool, “application specific” columns for commonly analyzed mixtures, for example, pesticides, dioxins, volatile organic compounds, fatty acid methyl esters, etc., were made available to laboratories lacking experience in systematic method development [19–21]. As a new millennium dawned complacency was being replaced by dependency as analysts ordered columns based on application notes and used instruments protected by service contracts. It was shocking how quickly both the average skill level of analysts working in gas chromatography laboratories declined and also that this was considered acceptable [13].

The above situation clearly has an impact on developments in gas chromatography, where they take place, and their ability to reach a critical mass of users. This is where ionic liquids come into the picture. They provide a range of properties complementary to conventional (nonionic) stationary phases with new challenges in column technology. Ionic liquids are solvents composed entirely of ions. The ionic liquids of most interest for gas chromatography are room temperature ionic liquids with a melting point or glass transition temperature below room temperature [3,4,22–27]. These were once a chemical curiosity, since most salts are solids at room temperature [22]. This picture changed dramatically with the identification of air-stable 1,3-dialkylimidazolium ionic liquids in 1992 and led to the discovery of the largest number of room temperature ionic liquids, which still dominate applications of ionic liquids in separation processes today [28]. Katritzky et al. [29] estimated that there are a possible  $10^{18}$  cation/anion combinations to create different ionic liquids. Thus, the number of potential ionic liquids is very large, and even though most of these combinations would not result in the formation of room temperature ionic liquids, and amongst this smaller number not all would have the necessary thermophysical properties to be used as stationary phases in gas chromatography, the number of potential ionic liquid stationary phases is still expected to be very large. By comparison, only a small number of these have been investigated so far as stationary phases [1–4].

## 2. Thermophysical properties of ionic liquids

For use as a stationary phase in gas chromatography the properties of ionic liquids of interest are melting point (and other phase transitions), vapor pressure, surface tension, thermal stability, viscosity, solubility in volatile organic solvents, and reactivity with different functional groups. The ionic liquid thermo database (NIST standard reference database #47) contains information for around 200 pure ionic liquids with most properties reported at atmospheric pressure and room temperature only [30]. This is only a drop in the bucket in terms of the number of known ionic liquids and a very small number compared with the theoretically possible number of ionic liquids. From such a small and selective database

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