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Discussion

Comments on the early history of gas chromatographic methods for oil analysis

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I am referring to the review article entitled Gas chromatographic methods for oil analysis, by Blomberg et al., published recently in this journal [1]. According to the abstract, the main intention of this paper was to review the developments since about 1985; however, it also reviews briefly the early history of this most important application of GC.

The paper presents a very thorough discussion, with 179 references. Unfortunately, however, its historical review provides an incorrect picture of the early developments, with significant omissions. The purpose of the present article is to correct these errors.

(i) According to the abstract, ''the main topics of interest are the introduction and decisive role of capillary GC.'' However, the discussion contains a number of factual errors and distortions. According to the paper, the possibility of capillary columns was predicted by A.J.P. Martin. Here this review gives an incorrect reference to his address at the 1958 Amsterdam Symposium [2]: actually, the quoted sentences are from his address at the 1956 London Symposium [3]. Periodically, one can find in the literature references to this ''prediction'' as a suggestion for open-tubular columns; however, this is far from the truth. In 1992, in a review paper [4] I tried to clear up once and for all this mistaken interpretation of Martin's statement, by showing the facsimile of his letter to M.J.E. Golay, written on 26 February 1982, on the occasion of Golay's forthcoming 80th birthday. In this letter Martin specifically stated that ''I have always kicked myself for not having tried to use a plain capillary tube as a column when I thought of the advantages of narrow tubes'' and ''I must say I had not anticipated the marvellous success the capillary columns had.'' I believe that no further comment is necessary.

It is unfortunate that the authors of the present review tried to perpetuate the myth of Martin predicting or proposing the open-tubular columns. As stated in a recent obituary [5], ''Archer Martin was one of the greatest scientific minds of the 20th century.'' He certainly does not need to be credited with development which did not originate from him.

Without any question open-tubular columns were invented in 1957–1958 by Golay and his fundamental paper was presented at the 1958 Amsterdam Symposium [6]. The present review specifically refers to three ''significant milestones'' of GC first presented at this symposium; however, it ignores Golay's paper. This omission is inexcusable: it is

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simply incomprehensible to handle him as an unperson in an article dealing with the evolution of capillary column gas chromatography.

(ii) Another omission can be found in the discussion of the early development of glass capillary columns. According to the present review the application of glass capillary columns was first reported by Grob toward the end of the 1960s. This is not true: the successful use of glass capillary columns was first reported by Desty et al. of British Petroleum, in 1959 [7], and machines permitting the preparation of glass capillary tubes for the use as GC columns were also described at that time [8,9]. What Grob did was to develop improved methods for the treatment of the glass capillary tube's inner wall. Also, the first real high-resolution gas chromatograms were shown not by Grob, but by Desty et al.: at the Third International GC Symposium organized by the Instrument Society of America, in East Lansing, MI, USA, in 1961, they showed the chromatogram of a the gasoline fraction (up to *n*-nonane) of a Ponca Crude sample [10]. A total of 122 peaks were obtained from which 78 were identified.

(iii) It should also be mentioned that high-resolution chromatograms obtained on metal capillary columns have been shown well before the references given in this review paper. I just briefly mention three, all from 1963:

Durrett et al. of Shell Oil (Texas) separated and identified 48 components of an isobutane–olefin alkylate sample, up to C_{10} [11];

Schwartz and Brasseaux of Shell Development (Texas) separated a 39-component C_5–C_8 hydrocarbon blend [12]; and

Martin and Winters of American Oil of Indiana successfully determined saturates through C_7, and alkylbenzenes through C_{10} in crude oils, obtaining 42 and 54 peaks, respectively [13].

(iv) According to the review article, ''the plate-number concept ... was developed by a distillation expert rather than by a chromatographer,'' and the reference given is to the paper by van Deemter et al. from 1956 [14]. This is, however, not true: the plate number concept was first described by Martin and Synge, in their fundamental 1941 paper [15], and this is in fact, specifically mentioned in the paper by Van Deemter et al. The theory developed by Van Deemter et al. had been named both by them and in the literature as the *rate theory*.

(v) The review article states that ''coupled columns were first reported in 1959, when Hughes et al. [16] described a three-stage gas chromatograph''. Actually, a three-stage gas chromatograph was first introduced by Perkin-Elmer in the summer of 1957 and described in detail at the Pittsburgh Conference, in Pittsburgh, PA, in March 1958 [17], and this instrument (the Model 188) had been commercially marketed for about 3 years, starting in 1958.

(vi) The review paper mentions among the highlights of the 1958 Amsterdam Symposium the first paper describing an automated gas chromatograph [18]. This paper described an automated process GC, for unattended use in pilot plants. However, this paper was certainly not the first describing such an instrument: by 1958, such instruments have already been available and in use in a number of American chemical and petrochemical plants. At the 1957 International GC Symposium of the Instrument Society of America, three papers dealt with process GC: two, by Ayers of Phillips Petroleum [19] and by Helms and Claudy of Perkin-Elmer [20] described in detail the unit developed jointly which was commercially available as the Model 184 of Perkin-Elmer, while Zinn et al. described [21] the instrument developed at Monsanto for their own use.

I realize that it was not the purpose of the quoted review article [1] to give an exhaustive review of early developments. However, even an abbreviated account of these developments should be reported correctly, without bias, omission or distortion.

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