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Letter to the Editor

Contribution to the measurement of prostaglandins by gas chromatography—mass spectrometry

Sir,

According to our previous paper [1], the prostaglandins (PG) $PGF_{2\alpha}$, PGE_2, PGE_1 and 6-keto-$PGF_{1\alpha}$ were measured as their methyl ester—methoxime—silyl ether derivatives by positive-ion chemical ionization with ammonia in the multiple-ion detection mode. Approximately 2000 analyses had been run over the gas chromatography column [30-m fused-silica from J&W Scientific (Rancho Cordova, CA, U.S.A.) coated with DB-1], then an improvement to the mass spectrometer (the Finnigan 4000 instrument was adapted for negative-ion chemical ionization) allowed the more sensitive measurement of negative ions. Therefore, methylation was exchanged for the formation of the corresponding pentafluorobenzyl derivatives and the ammonia was replaced with methane for the chemical ionization. For the tetradeuterated prostaglandins, ions of *m/z* 573 for $PGF_{2\alpha}$, *m/z* 528 for PGE_2 and *m/z* 618 for 6-keto-$PGF_{1\alpha}$ were detected. The ratio of the peak areas was approximately 100:50:80 for *m/z* 573:528:618. In addition to the samples used for testing the new method, other different samples were injected on to the column which is now nearly two years old. As a standard for testing the gas chromatographic—mass spectrometric conditions a sample of 10 pg/μl deuterated $PGF_{2\alpha}$ was used. Under good conditions a signal-to-noise ratio of 4:1 was obtained from 10 pg; a dirty ion source needed a splitless injection of 100 pg.

During subsequent weeks it was found that the results became increasingly worse. A 100-pg amount of $PGF_{2\alpha}$ gave a signal, but more than 10 ng of PGE_2 remained undetectable and the ratio of the peak areas became increasingly different from that originally observed, changing to $100:<1:<10$ for *m/z* 573:528:618.

The fact that relatively satisfactory results were obtained from $PGF_{2\alpha}$, whereas the peak areas of the two substances transformed into methoximes disappeared, made it probable that derivatization problems caused these losses. This opinion was supported by the observation that changes in the derivatization procedure were sometimes accompanied by variations in the results. However, this was misleading.

Finally, the old column was replaced with a new one (coated with DB-5) and

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it was astonishing to observe that a large increase in sensitivity was accompanied by a change in the relative intensities of the three ions, the ratio of peak areas now being approximately 1:1:1 for *m/z* 573:528:618. The increase in sensitivity was significant as 500 fg were now detected with a signal-to-noise ratio of 10:1, after a previous injection of 10 μl of bistrimethylsilylacetamide followed by 10 μl of *n*-hexane.

These observations prove that active centres arising on old columns can cause not only a general loss of substances but also a selective destruction of molecules.

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