Journal of Chromatography, 474 (1989) 145–148
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 21 359

IMPROVING THE ION CURRENT STABILITY OF A THERMOSPRAY SOURCE BY IMPROVING THE CONTROL OF THE VAPORIZER TEMPERATURE AND SOLVENT FLOW-RATE

WIM GENUIT* and HERMAN VAN BINSBERGEN
Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research B.V.), Badhuisweg 3, 1031 CM Amsterdam (The Netherlands)

SUMMARY

The original time-proportional vaporizer temperature control system of the thermospray source has been changed into a system based on phase-angle control, which enhances the vaporizer temperature stability, and hence the ion current stability of the source. When combined with a solvent pressure stabilization system, this new temperature control system stabilizes the vaporizer temperature to within 0.1°C of the set value.

INTRODUCTION

Partial evaporation and break-up of a liquid flow into small droplets, as occurs in a thermospray liquid chromatography–mass spectrometry (LC–MS) interface, inevitably involve statistical fluctuations, which affect the stability of the ion current output from the thermospray source. However, small variations in the vaporizer temperature[1] or in the LC eluent flow-rate[2] also have a large effect on ion current stability.

Conventional time-proportional control systems tend to induce variations in vaporizer temperature owing to the pulsed mode of heating, which allows the vaporizer capillary to cool between repetitive pulses, and to electrical feedback of the heating current pulses through the thermocouple spot weld. The rapid fluctuations in ion intensity resulting from these variations hamper the optimization of thermospray operating conditions, and make accurate mass calibration and quantitation from thermospray data even more problematic.

This paper deals with a temperature stabilization system based on phase-angle control, which provides a uniformly time-distributed heating power. This system yields a marked improvement in vaporizer temperature and ion-current stability, compared with the time-proportional control system. It is shown that with this new temperature control system, most of the residual temperature variation is due to LC pump pulsation and can be eliminated by stabilizing the solvent flow-rate.

0021-9673/89/$03.50

INSTRUMENTAL

A Waters Assoc. 600MS multi-solvent delivery system, provided with a flow-rate stabilization option, is used to pump a tuning solution consisting of methanol–water (1:1) with the addition of 0.05 *M* ammonium acetate buffer and 100 ppm (v/v) of polyethylene glycol PEG 400 at a flow-rate of 1.5 ml/min.

The mass spectrometer is a Finnigan 4500 TSQ quadrupole mass spectrometer equipped with a Finnigan-MAT thermospray LC–MS interface.

Initially, the interface exhibited very poor temperature stability, which was attributed to an over-dimensioned power circuit. The maximum heating power was then reduced by putting a diode into the circuit, cutting off half of each alternating current period. While this modification gave some improvement in temperature stability, rapid fluctuations of several degrees Celsius were still observed.

In the experiments described below, either the modified time-proportional control circuit, or a phase-angle control system, made up of an 818P programmable controller and a 425 phase-angle thyristor unit (both from Eurotherm, Worthing, U.K.), is used. Fig. 1 shows the two circuits with their different control characteristics. Time-proportional control varies the on/off ratio within a control cycle period which is much longer than the 10-ms power cycle period (corresponding to a 50-Hz line frequency). On a 10-ms time scale, a time-proportional system delivers its heating power in pulses. Phase-angle control varies the on/off ratio witin each power cycle period. Therefore, on the same 10-ms time scale phase-angle control provides a much more uniformly distributed heating power.

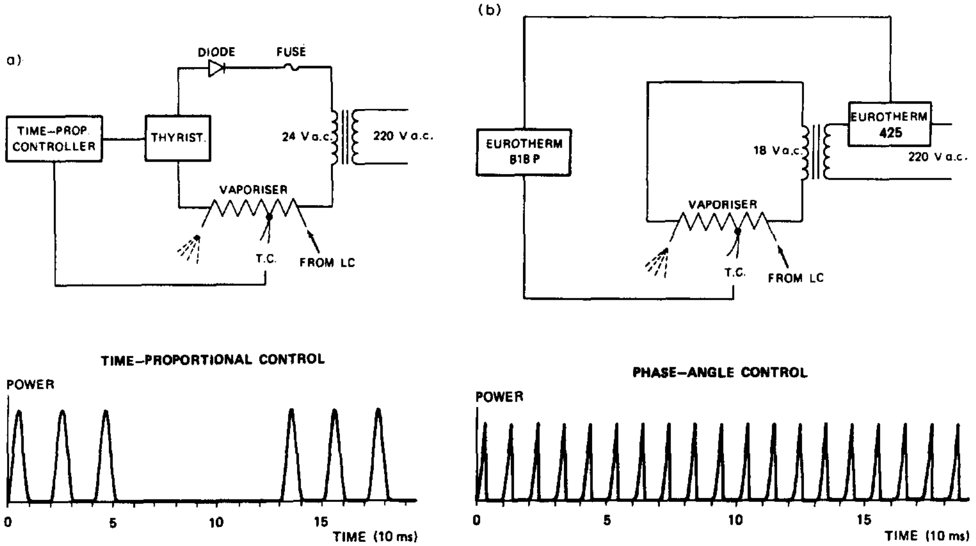

Fig. 1. (a) The modified Finnigan time-proportional vaporizer temperature control circuit. (b) The new phase-angle control circuit.

RESULTS

Fig. 2 shows the thermospray mass spectrum of the tuning solution. Ions above *m/z* 150 correspond to the protonated PEG oligomers (odd-numbered series) and the respective ammonium adducts (even-numbered series).

For the ion current stability tests, the quadrupole mass filter is set manually at *m/z* 344, and the vaporizer temperature and ion current are recorded simultaneously by a two-pen recorder. A typical result is shown in Fig. 3. The first part (A) was

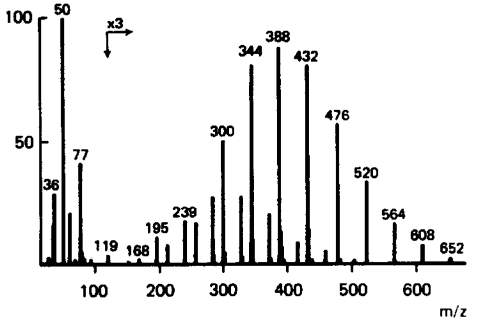

Fig. 2. Thermospray mass spectrum of the PEG 400 tuning solution.

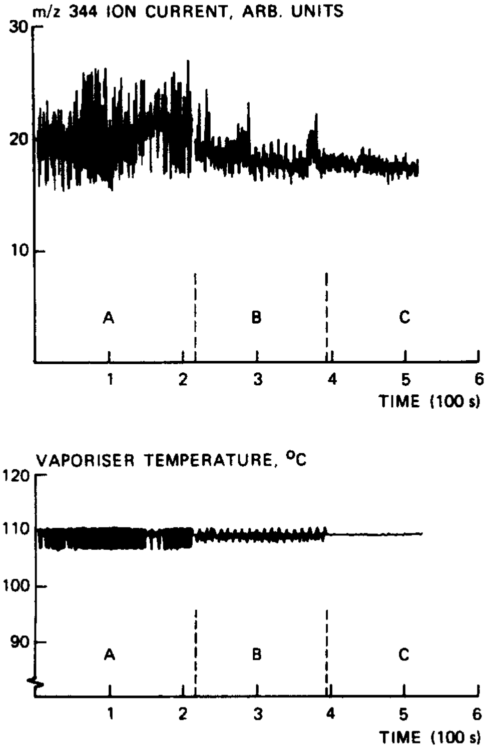

Fig. 3. Vaporizer temperature and *m/z* 344 ion current trace as a function of time. A, Time-proportional heating system; B, phase-angle heating system; C, phase angle heating system + flow-rate stabilization.

obtained using the time-proportional control, without flow rate stabilization. The vaporizer temperature, optimized for a maximum *m/z* 344 ion current, oscillates rapidly between 107 and 110°C, and the ion current trace shows corresponding fluctuations. Part B was recorded using the new phase-angle control system and without flow-rate stabilization. The high-frequency variations in temperature and ion current are largely reduced, compared with A, and the slow variations on an approximately 10-s time scale, observed in both traces, are exactly in phase with the piston movements of the solvent pump. This result illustrates the inadequately of piston pulse-damping devices in normal LC pumps for thermospray LC–MS work, at least when they are operating in the column bypass mode, or as a post-column buffer addition pump. In part C, using phase-angle temperature control combined with solvent flow-rate stabilization, this slow variation is eliminated, and the vaporizer temperature is stable to within 0.1°C of the set value. The corresponding ion current trace shows the remaining thermospray noise.

These experiments were repeated a few times with different crimped vaporizer tips. Although the vaporizer characteristics, such as optimum temperature and temperature stability, vary somewhat from one tip to another, the results are similar in that the stability is greatly enhanced by the new temperature control. Also, the vaporizer temperature is found to be much less critical, the vaporizers operating steadily in a wide temperature range.

CONCLUSIONS

Poor stabilities of vaporizer temperature and solvent flow-rate are important sources of ion current fluctuations in a thermospray LC–MS interface. Temperature stabilization by a phase-angle controlled system gives a significant stability improvement over the pulsed time-proportional systems. Temperature variations induced by pump pulsation can be eliminated by applying flow-rate stabilization.

REFERENCES

1 R. H. Robins and F. W. Grow, *Rapid Commun. Mass Spectrom.*, 2 (1988) 30.
2 M. L. Vestal and G. J. Fergusson, *Anal. Chem.*, 57 (1985) 2373.