Short communication

# Occasional sub-ambient temperature programming performed in two "isothermal" gas chromatographs[☆]

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## Abstract

By temporarily inserting large thermal masses into the column baths of existing "isothermal" gas chromatographs, linear temperature ramps have been obtained from constant energy inputs. Typically, the rise of temperature could be held linear (within ±3°C) over a more than 100°C range. Since the metal inserts can be cooled before insertion, this approach extends thermal programming to subambient temperatures (e.g. down to −130°C in one case of this study). While such a temporary arrangement cannot compete in speed and convenience with gas chromatographs specifically designed for electronic control and liquid nitrogen cooling, it offers the occasional user an alternative that is inexpensive to assemble and simple to use.

## 1. Introduction

Gas chromatographs (GCs) that can be programmed at subambient temperatures are available from several GC manufacturers. These should obviously be employed if subambient temperature programming is the prime analytical task.

For most GCs, it is not. Yet occasions do arise when the analyst would like an innately isothermal GC to perform subambient and/or superambient temperature programming, say in order to accommodate an infrequent but insistent customer, or to meet an unusual but unavoidable research demand. Two typical cases from our group —whose main concern is detec-

tor development and trace organic analysis— may illustrate the point.

In the first case, the GC —a recently acquired, dedicated Shimadzu Model GC-8AIE— carried an electron-capture detector and had therefore little need and indeed no facility for temperature programming. After using it for some studies of electron-capture mechanisms [1], we connected its column to a laboratory-made sequential three-detector [1] combination (existing electron-capture plus reactive-flow luminescence [2] plus flame ionization detector). To test this tridector's performance in multi-channel correlation chromatography, we wanted to observe the behavior of some highly volatile analytes; and we also wanted to trace these analytes in a complex matrix such as gasoline. This obviously required a thermal program —and one that would start at subambient temperature.

In the second case, the GC —a Hewlett-Pac-

kard Model 700 with flame ionization detector—hailed from so early a chromatographic time that, although it already sported a fan, it still lacked a thermostat. Consequently, the isothermal temperatures of its column bath had to be slowly established as steady-state outcomes of the contest between the heat gain from its constant-voltage resistance coil and the heat loss to its walls and the lab environment. For a student project [3] involving volatile air pollutants, we decided to press this surplus item from our undergraduate organic chemistry laboratory into service, and lend it subambient-temperature programming capability.

The question was how. Modern GCs have very small heat capacities to permit fast temperature adjustment with shallow gradients in the air of the column bath. If they lack a temperature-programming controller, the only possibility to introduce a thermal ramp is to go "ballistic". (Despite this historic name, a "ballistic program" is really no "program" at all: the operator simply aims at some high isothermal setting and allows the temperature to shoot up.) In most isothermal instruments, therefore, the available ballistic program is too fast, not capable of a change in rate, and severely non-linear. In other words, it is of little or no practical value.

Despite the non-linearity of a ballistic program, its heat *input* is still roughly constant (and usually going at full tilt). The *non*-linearity of its temperature rise thus derives from the increasing temperature differential —and hence the increasing rate of heat transfer— from the inside (column-bath) air to the *low* thermal-capacity surrounding walls with associated structures and on to the outside air. However, if the column bath could be given a *high* thermal capacity, the "ballistic" temperature rise should come closer to being linear. In other words, most of the heat input could then enter a massive thermal sink (which would be part of, or would be situated in, the column bath); provided that heat transfer to this sink were made a reasonably fast process.

Simpler expressed, it should be possible to insert large pieces of metal into the column bath, with enough structure in the metal so the circulating air could heat them fast and efficiently. If

these pieces of metal were precooled, a subambient temperature program would result.

Is such a procedure feasible? Is it cheap to install and easy to run? How large is its linear temperature range? How low a temperature can it conveniently reach?

## 2. Experimental

In order to answer these and other questions, larger pieces of structured, blackened aluminum were strung together in a form that, cold or hot, could be easily moved in and out of the column bath. The assembled piece for the Shimadzu weighed about 8 kg, the three pieces for the Hewlett-Packard together 4.5 kg. That seemed adequate for a first try. It also allowed us to compare two substantially dissimilar thermal sink capacities operating in two roughly similar column-bath volumes.

The Hewlett-Packard's isothermal temperature is *not* under thermostatic control; it is the steady-state, slowly attained outcome of a constant voltage being imposed on the heater. Setting a higher voltage would therefore increase the slope of the ballistic or thermal-sink-moderated temperature ramp: a feature that conveniently coincided with what we had in mind for the instrument.

In contrast, the Shimadzu's isothermal temperature is controlled by a thermostat with full-voltage input to the resistance heater: if left alone this would allow only *one* heating rate (short of changing the mass of the aluminum insert). The Shimadzu's resistance heater was therefore connected to an external Variac (variable autotransformer) such that either the instrument's thermostat controlled the time, or the external Variac controlled the magnitude, of the voltage imposed on the heater. Even nowadays, Variacs are occasionally used as GC inputs, although they usually serve a different purpose (cf. Ref. [4] and references cited therein). Just to be on the safe side, a laboratory-made digital thermometer was set up to cut off all power to

the heater if the column bath temperature should rise beyond a given threshold.

The aluminum inserts were cooled by solid water or liquid nitrogen. The Shimadzu column was an 80 cm × 2.5 mm I.D. borosilicate tube filled with 5% OV-101 on Chromosorb W, 45–60 mesh; the Hewlett-Packard column a similar 160 cm-long tube filled with 5% OV-101 on Chromosorb W AW, 100–120 mesh. Other conditions were similarly crude and conventional.

## 3. Results and discussion

It is obvious that, during the program, the temperature of the aluminum inserts will lag that of the constantly heated air circulating in the column bath. The extent of the lag must depend on the thermal mass of the aluminum and on the rate of its heat exchange (as well as on the power input). Clearly, the structure of the aluminum heat sink —its surface area and radiative ef-
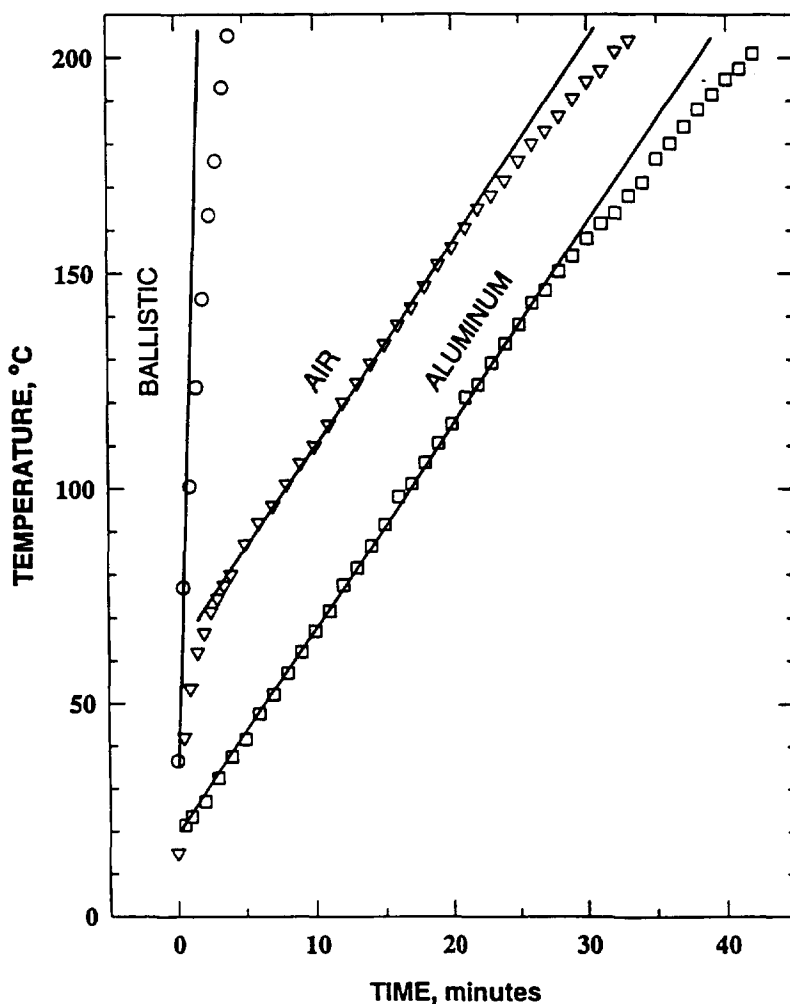


Fig. 1. Temperature rise in column bath air and aluminum insert (at an arbitrarily chosen location), as compared to a "ballistic" program (i.e. without aluminum insert). The 8-kg aluminum insert was cooled with ice cubes in the sink. Power input: 90% of line voltage (Variac). Shimadzu gas chromatograph.

ficiency, its local thickness, its extent of inter-
action with the air stream, etc.— will all in-
fluence the overall thermal exchange rate.

Given the but occasional task the aluminum
inserts have to perform, we did not attempt to
optimize their mass, surface, interactions with
the air flow, etc. We simply assembled various
pieces of aluminum, subjected them to some
milling and drilling (to improve air-aluminum
contact), and blackened them. Partly due to
available bath geometry and partly due to ex-
perimental design, the Shimadzu's insert was far
heftier than the Hewlett-Packard's.

For general interest, the temperature lag be-
tween the aluminum insert and the bath air was
determined in both instruments, with a relatively
high programming rate ensuring a pronounced
lag. Figs. 1 and 2 show the results obtained with
ice-cooled inserts from the Shimadzu and the

Hewlett-Packard, respectively. They offer no
surprises. The thermal lag is about 42°C in the
Shimadzu, about 15°C in the Hewlett-Packard.
The difference between the two relates mainly to
the different mass of the aluminum inserts (8 kg
in the Shimadzu and 4.5 kg in the Hewlett-
Packard) and to the different power output of
the heaters.

Figs. 1 and 2 also illustrate the limits of linear
behavior. The straight (and parallel) lines show
that the air temperature rises in a linear manner
over about 100°C in both instruments. For the
occasional need of programmed chromatography
—and only the *occasional* need we want to
address here— this range should be more than
adequate. Where the heat-sink moderated pro-
grams do deviate from linearity, the deviation
—as long as it is reproducible— is unlikely to
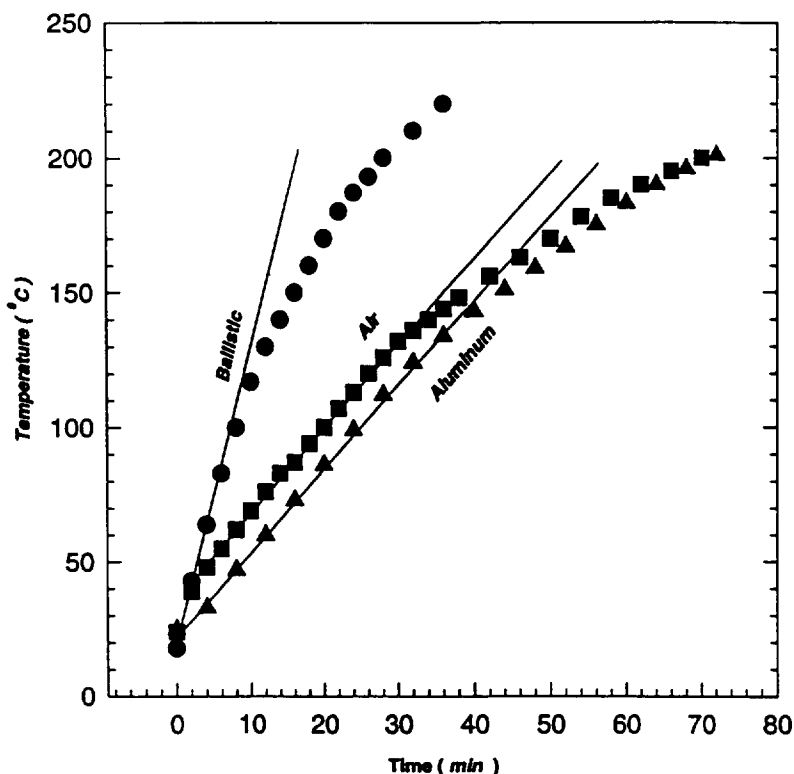hurt most analytical tasks. In view of the lower



Fig. 2. Similar to Fig. 1, but Hewlett-Packard gas chromatograph. Power setting "8" (on a scale of 10). Three aluminum inserts
of total mass 4.5 kg were used.

separation numbers ("Trennzahlen") at higher temperatures, a gradual slackening of the temperature rise may sometimes be even desirable.

For special needs it is possible to obtain lower temperatures and an even longer linear range. Fig. 3 shows an example. The Hewlett-Packard column bath and the inserts are cooled with liquid nitrogen. The program starts at −130°C and proceeds in linear fashion over a 150°C range.

It should be mentioned, however, that such heroic measures can have side effects. If sizeable amounts of water from the atmosphere freeze on exposed metal parts (as they are wont to do in the Shimadzu), the temperature rise will kink at 0°C and possibly even at 100°C.

Since this study was designed to satisfy temporary needs by a make-shift approach, no constructive measure was taken to cope with the problem of water condensation; nor was any sort of mechanical or procedural optimization attempted. Similarly, no attempt was made to measure or modify any —possibly even pronounced— temperature differences in different regions of the circulating column bath air (which could lower the resolution of high-performance columns).

The make-shift procedure did indeed satisfy our temporary need. Fig. 4 presents as a typical example the rough separation of gasoline. Gasoline is used here as a model hydrocarbon matrix under low-resolution conditions (i.e. on an 80-cm column packed with 45–60-mesh particles), which can potentially interfere with the response of highly volatile analytes in the tridector [1]. The early hydrocarbon peaks are well spread out, as desired.

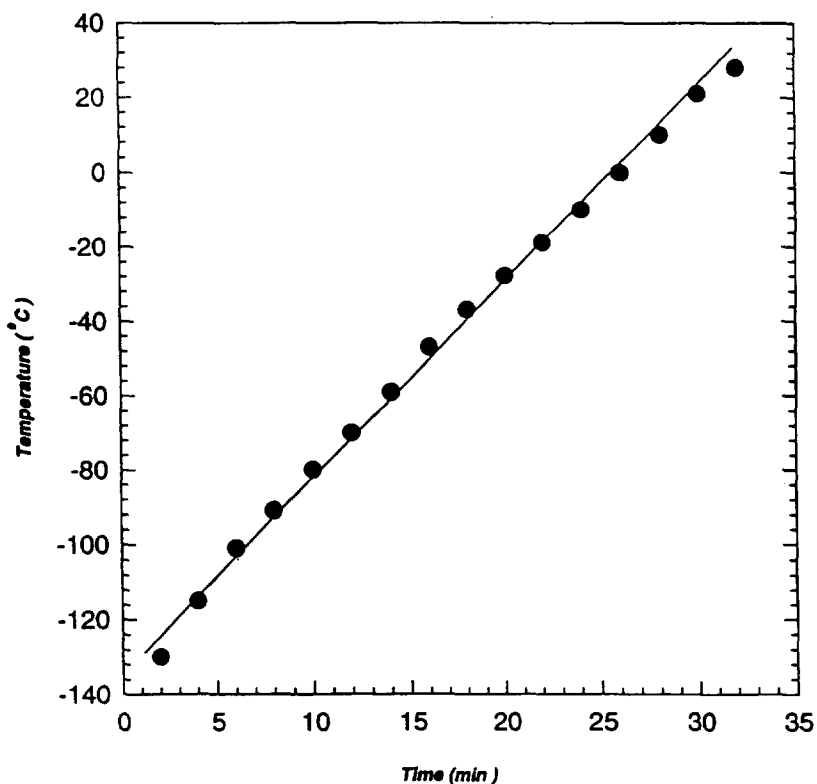While such separations can be more easily and



Fig. 3. Subambient temperature ramp in the Hewlett-Packard gas chromatograph. Column bath and aluminum inserts precooled by liquid nitrogen. Power input setting: 8.
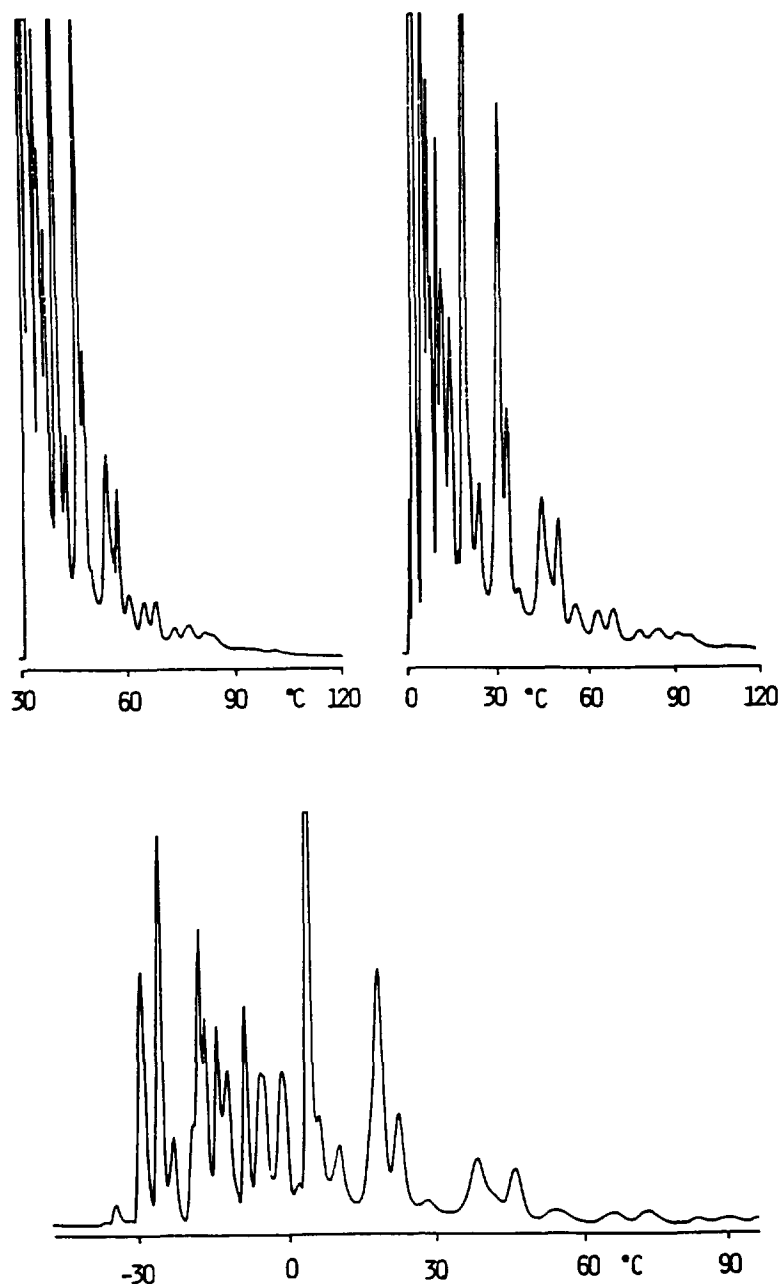
Fig. 4. Temperature-programmed chromatographies of "regular"-brand gasoline in the Shimadzu gas chromatograph, starting at different temperatures. Power input: 90% of line voltage.

more efficiently (though also more expensively) carried out on a liquid nitrogen-cooled commercial GC, inserting a thermal sink into an existing isothermal (or even programmable) GC provides an easy way out for the analyst who faces an unexpected but temporary requirement for subambient programming. Beyond analysis, the dampening effect of the large thermal mass may come in handy if the operator should want to avoid, for whatever purpose, the short-term

discontinuities (cycling) of conventional heating controls. A further and —at least in our labs— major advantage of using a heat sink designed to be inserted and removed for each subambient or superambient temperature-programmed run is that *one* insert can serve the occasional needs of *several* similarly dimensioned gas chromatographs. To wit, we use the same insert on three different Shimadzu model-8 units carrying different detectors and associated equipment. One heat sink thus provides both programming capability to an electron-capture instrument and subambient capabilities to two (temperature programmed) flame-photometric instruments. Furthermore, a typical heat sink can be designed to serve even differently sized and shaped column baths.

We should add that metal inserts of high cooling capacity are such a "natural" that it would come as no surprise to us if similar units had been used before— in chromatography, analytical chemistry, or other scientific disciplines. Searching a vast literature for devices of a self-evident nature can, however, take a long time. Worse, it can produce false negatives and, in turn, induce false notions of novelty. We prefer therefore —just in case— to pre-emptorily extend our apologies to kindred tinkerers for any unintentional failure on our part to recognize their earlier contributions.

## Acknowledgements

## References

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