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## Note

### Effect of ligand doping on the gas chromatography of the trifluoroacetylacetonates of chromium(III), aluminium(III) and iron(III)\*

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The gas chromatography (GC) of trifluoroacetylacetonates has been extensively studied<sup>1-26</sup>. Methods for determining several metals, *e.g.*, chromium, aluminium and beryllium, as their trifluoroacetylacetonates in a wide variety of materials have been developed<sup>7-26</sup>. The main problem associated with the determination of trifluoroacetylacetonates is their lack of stability under GC conditions. Dissociation of the chelates results in a smaller peak and a build-up of metal ions which may react to form trifluoroacetylacetonates again and elute during subsequent injections<sup>6,10</sup>.

To reduce dissociation, Fujinaga and co-workers<sup>27-30</sup> added trifluoroacetylacetonone [H(tfa)] to the carrier gas of a GC system equipped with a thermal conductivity detector (TCD), and found an improvement in the response of some trifluoroacetylacetonates, especially those of the rare earths.

This paper reports the doping of a relatively small amount of trifluoroacetylacetonone into the carrier gas of a GC system using a flame-ionization detector (FID).

#### EXPERIMENTAL

A Perkin-Elmer 3920 gas chromatograph equipped with an FID was used. The column was a 3 ft. × 2 mm I.D. stainless-steel tube packed with 5% OV-101 on Chromosorb W, DMCS treated, 80-100 mesh. It was kept at 125°C for Cr(tfa)<sub>3</sub> and Fe(tfa)<sub>3</sub>, and at 115°C for Al(tfa)<sub>3</sub>. The carrier gas was helium at a flow-rate of 25 ml/min. Chromium, aluminium and iron trifluoroacetylacetonate were injected as solutions in hexane, the usual volume introduced being 1 μl.

Trifluoroacetylacetonone was introduced into the GC system by routing a variable fraction of the carrier gas stream over a small pool of the dopant. This was done by using a combination of valves as shown in Fig. 1. Valves 1 and 2 were needle valves (Nupro, B-2MG) whereas valve 3 was an on-off valve (Whitey, B-ORS2). Under doped conditions, both valves 1 and 3 were fully open, the fraction of helium flowing over the ligand being controlled solely by valve 2. Valve 3 was used to cut off the H(tfa) stream such that setting on the needle valve 2 needed not be disturbed when the non-doped mode was run. The maximum trifluoroacetylacetonone introduction rate that could be tolerated was about 50 μg/min or 2 μg/ml of helium, corresponding to opening valve 2 by 2.75 turns in the present set-up.

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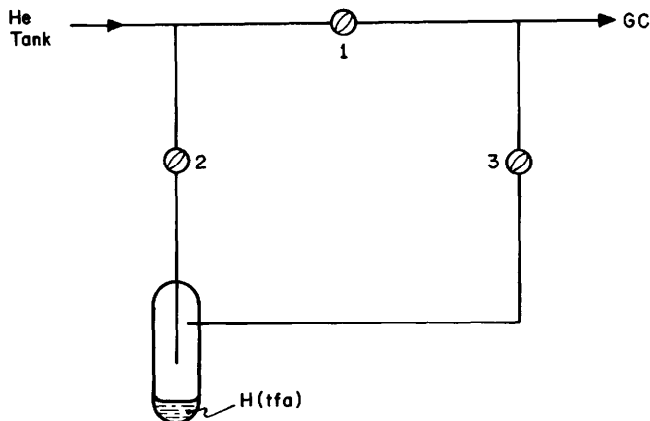


Fig. 1. Doping arrangement.

## RESULTS AND DISCUSSION

The amount of H(tfa) that could be introduced into the GC system was limited because the FID is much more sensitive than the TCD. Further, the FID lacks a reference cell, which the TCD has, for zeroing the response due to trifluoroacetylacetonone in the carrier stream. Above  $2 \mu\text{g}$  of H(tfa) per ml of helium, the electrometer bucking could no longer bring the baseline current down to a workable level. Such a system would, however, allow a study of the effect of the addition of trace levels of H(tfa) on nanogram amounts of trifluoroacetylacetonates.

On-column decomposition of the trifluoroacetylacetonates is evident when H(tfa) is absent from the carrier stream. Except for  $\text{Cr}(\text{tfa})_3$ , the response of the chelates increases with repetitive injection and then levels off. Reproducible injections can be obtained when this plateau region is reached. The number of injections needed to attain the plateau stage varies with each trifluoroacetylacetonate: aluminium requires about three and iron about five. The reproducibility of the chromium trifluoroacetylacetonate response is always within the repeatability of syringe injection. Decomposition of this chelate is only obvious when concentrated H(tfa) solution is injected immediately after elution of the chelate peak (see below).

Fig. 2 shows the effect of H(tfa) on the responses of chromium, iron and aluminium trifluoroacetylacetonates: the response increases with increasing amounts of H(tfa) in the carrier gas. [The concentration of H(tfa) in the carrier gas is expressed as the number of turns that valve 2 is opened. The exact relationship between the two is unknown; however, it is evident that the former increases with the latter.] Similar enhancements, mostly with trifluoroacetylacetonates of the rare earths, have been described in the literature. These were attributed to suppression of the dissociation of these rather labile chelates due to the presence of ligand vapour in the GC system<sup>27-30</sup>. It is interesting to note here that the response for two of the most stable trifluoroacetylacetonates, chromium and aluminium, also increases in the presence of trifluoroacetylacetonone. Further, the increase with  $\text{Cr}(\text{tfa})_3$ , the more stable of the two, is higher. The number of injections required before a reproducible response can be obtained decreases from three to two for aluminium and from five to three for iron

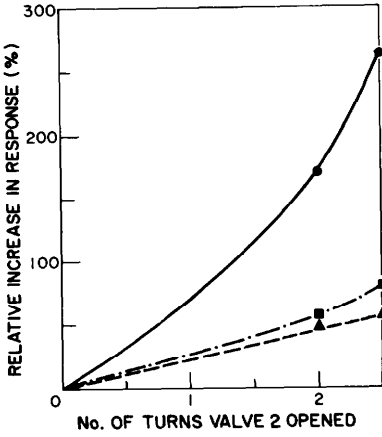


Fig. 2. Effect of H(tfa) doping on the responses of chromium (●), aluminium (▲) and iron trifluoroacetylacetonates (■).

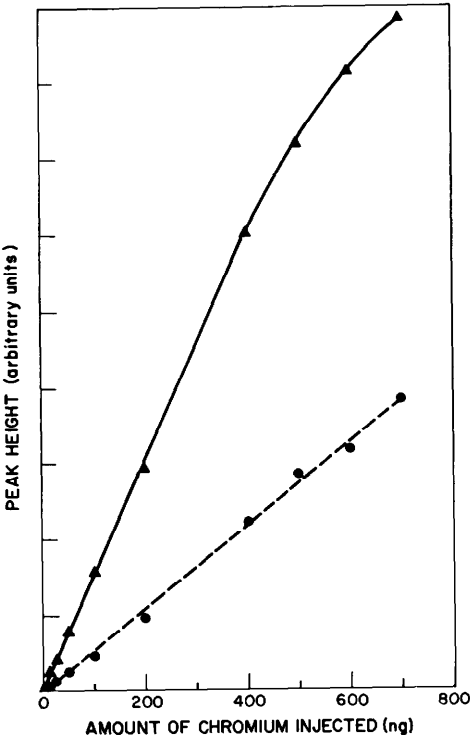


Fig. 3. Calibration graphs for chromium trifluoroacetylacetonate: ▲, with H(tfa) doping; ●, without H(tfa) doping.

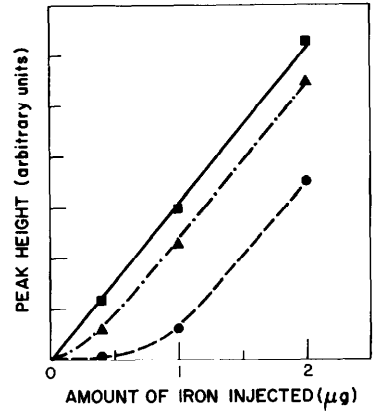


Fig. 4. Effect of H(tfa) doping on the calibration graph for iron trifluoroacetylacetonate: ●, no H(tfa); ▲, valve 2 opened by 2 turns; ■, valve 2 opened by 2.5 turns.

trifluoroacetylacetonate. As an aside, enhancement for  $\text{Cr}(\text{tfa})_3$ , although to a smaller extent, is observed when acetone is doped into the system. Whether the enhancement seen here is due solely to suppression of chelate dissociation is debatable and the matter is now under investigation.

Fig. 3 shows calibration plots of chromium trifluoroacetylacetonate obtained both with and without trifluoroacetylacetonate doping. The minimum detectable amount (the amount that would give a response equal to twice the noise level) in both instances is about 5 ng. This is because the noise level in the doped mode, due mainly to fluctuations of local ligand concentration, also increases with increasing concentration of  $\text{H}(\text{tfa})$ . The most dramatic improvement occurs with iron, as illustrated in Fig. 4.

Another important aspect of ligand doping is the decrease in memory effect. Metal ions retained in the GC system may react with available ligand in subsequent runs to form trifluoroacetylacetonates which would then elute. An easy way to assess the degree to which this happens is to inject a relatively concentrated  $\text{H}(\text{tfa})$  solution immediately after elution of the metal trifluoroacetylacetonate of interest. Table I lists the results of such a study both with and without ligand doping. The beneficial effect of having a trace amount of  $\text{H}(\text{tfa})$  in the carrier gas is evident. It should be noted that the extent of the memory effect parallels the stability of the trifluoroacetylacetonates with  $\text{Cr}(\text{tfa})_3$ , the most stable chelate, showing the least effect. Reduction of memory effect brings about an improvement in precision and hence ensures more reliable results.

TABLE I  
MEMORY EFFECT OF TRIFLUOROACETYLACETONATES

Metal ion	Memory effect (%) <sup>*</sup>	
	Without $\text{H}(\text{tfa})$ doping	With $\text{H}(\text{tfa})$ doping <sup>**</sup>
Cr	1.9	1.0
Al	9.0	3.2
Fe	33.0	3.6

<sup>\*</sup> Expressed as [peak height of trifluoroacetylacetonate in subsequent  $\text{H}(\text{tfa})$  injection/peak height of trifluoroacetylacetonate] · 100.

<sup>\*\*</sup> 2  $\mu\text{g}$  of  $\text{H}(\text{tfa})$  per ml of helium.

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