# The Gas Chromatographic Determination of Carbonyl Compounds as Their Thiosemicarbazone

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The gas chromatographic determination of carbonyl compounds in a contaminated air sample *via* their thiosemicarbazone was studied. As the method utilizes the selective detectability of the flame photometric detector for the sulfur compound, the isolation of the sulfur-containing derivatives of the carbonyl compounds is not required; this eliminates the inaccuracy stemming from the isolation of the derivatives from the sample solution. The isolation and subsequent regeneration of the carbonyl compound was carried out *via* the thiosemicarbazone metal complex; this affords a practical method of preparing the sample required for the identification of the individual carbonyl compound.

The identification and quantitative determination of carbonyl compounds is a commonly encountered problem in air-quality analysis—for example, the analysis of the carbonyl compounds in automobile exhausts and in concentrated air samples.

Derivatization *via* 2,4-dinitrophenylhydrazine (DNPH) followed by subsequent gas chromatographic analysis, has been widely used for carbonyl analysis. The carbonyl DNPH derivatives have been analyzed directly by gas chromatography,[1-6] or, after the hydrolysis of the carbonyl DNPH derivatives by heating them with mineral or organic acid, the regenerated carbonyl compounds have been analyzed.[7-8] The gas chromatographic analysis of the carboxylic acids produced by the ozonization of the carbonyl DNPH has also been reported.[9]

In this study, the carbonyl compound was converted into its thiosemicarbazone, and the latter sulfur-containing derivative was detected by means of a flame photometric detector (FPD). As the selective detectability of FPD for the sulfur compounds permits the selective determination of the carbonyl thiosemicarbazone in a contaminated sample—for example, in auto exhaust or in concentrated air sample which contains foreign compounds other than the carbonyl compounds, the isolation of the carbonyl compound derivative from the foreign compounds is not required. This fact, in conjunction with the specific and quantitative thiosemicarbazone formation reaction, could eliminate the inaccuracy stemming from the separation or extraction of the carbonyl compound derivative which is encountered in the direct carbonyl DNPH method.

Further, the unique property of thiosemicarbazone to form an insoluble metal complex with heavy metal salts can be utilized for the isolation, followed by regeneration, in the identification of the individual carbonyl compound by GLC-Mass analysis, which requires the isolation of the carbonyl compounds from other impurities, *e.g.*, hydrocarbons.

## Experimental

*Thiosemicarbazones.* The general procedure for the preparation of all the thiosemicarbazones listed in Table 2 was as follows. The carbonyl compound (0.01 mol) was dissolved in 10 ml of 95% ethanol, and then approximately 0.2 ml of glacial acetic acid and 0.9 g (0.01 mol) of thiosemicarbazide were added. The reaction mixture was stirred at room temperature until the thiosemicarbazide dissolved (it usually took 0.5—1 hr) and was then refluxed for 0.5 hr. The solvent was evaporated under reduced pressure, and the crude product was recrystallized from 50% ethanol or methanol.

*Determination of the Response Factors and the Relative Retention Values of Thiosemicarbazones.* Gas chromatography was done by means of a Micro Tek Instruments Corp. Model 160 gas chromatograph equipped with a flame photometric detector and a 4 mm i.d.$\times$1 m glass column packed with Diasolid ZT (Silicone). The other analytical conditions are described in Tables 1 and 2.

In the determination of the response factors of the thiosemicarbazones listed in Table 1, the sample solution was prepared by mixing 1 ml of the solution of thiosemicarbazone ($1\times10^{-4}$ mol) in 10 ml of ethanol, with 10 $\mu$l of the internal standard solution (di-*n*-amyl sulfide $1\times10^{-4}$ mol in 3 ml ethanol). The peak areas of each thiosemicarbazone and internal standard sulfide were determined by means of a digital integrator, while the response factor ($F_i$) was calculated by the use of the following equation:

$$F_i = A_s/W_s \times W_i/A_i$$

where: $A_s$ and $W_s$=peak area (log) and the weight of the internal standard respectively, and $A_i$ and $W_i$=peak area (log) and the weight of thiosemicarbazone respectively.

The relative retention values ($\alpha$) of the thiosemicarbazones listed in Table 2 were calculated by means of the following equation:

$$\alpha = (X_1-X_0)/(X_s-X_0)$$

where $X_0$, $X_s$, and $X_1$ are the distances (in time) from the point of injection to the maximum of the chromatographic peaks of the solvent (ethanol, detected by means of a FID monitor coequipped with FPD), the internal standard (di-*n*-amyl sulfide), and thiosemicarbazone respectively.

*Separation and Regeneration of the Carbonyl Compounds via the Thiosemicarbazone/$AgNO_3$ Complex.* A solution of silver nitrate (0.01 mol) in 5 ml of distilled water was added to a thiosemicarbazone (0.01 mol)/EtOH solution. After 30 min's stirring at room temperature, the reaction mixture was evaporated to dryness under reduced pressure. The residual, black-colored solid was washed with a hydrocarbon solvent (*e.g.*, *n*-hexane) and then dissolved in 20 ml of ethanol; 5 ml of 6 M-HCl was added, and the reaction mixture was stirred for 1 hr under refluxing, cooled, and filtered. The content of the carbonyl compound in the filtrate was determined by the gravimetric 2,4-dinitrophenylhydrazine method.

## Results and Discussion

The thiosemicarbazones listed in Table 2 were prepared by Campaigne's method.[11] Unlike semicarbazide, the thiosemicarbazide is stable in its free form, and in the presence of a small amount of glacial acetic acid, the reaction proceeds readily at room temperature and the thiosemicarbazone formation reaction has the minor possibility of a side reaction. The thiosemicarbazone-formation reaction with the 15 carbonyl compounds listed in Table 2 proceeded readily at room temperature: an initially insoluble crystal of thiosemicarbazide dissolved in 0.5—1 hr, and either a clear solution or a crystal of newly-formed thiosemicarbazone was obtained. The small deviations in the melting points between the crude and the purified product indicated the absence of any side reaction or isomer formation.

It has been reported that, in the direct gas-chromatographic analysis of the carbonyl DNPH, the reproducibilities were poor, the response factors varied with the concentration, spurious decomposition peaks or double peaks hampered the analysis, and a homologous series of carbonyl DNPH derivatives had widely varying responses per mole when detected by FID.[1,2] All of these results indicated that the higher-molecular-weight carbonyl DNPH derivative resulted in a varying loss of the derivatives through thermal decomposition in the gas-chromatographic system.

However, the carbonyl thiosemicarbazone, which has a smaller molecular weight than the carbonyl DNPH, makes possible milder analytical conditions, which minimize the thermal decomposition of the derivatives. In this study, column temperatures of 125—200 °C, inlet temperatures of 150—200 °C, and a detector temperature of 170 °C were used, because the melting points and the decomposing points of the 15 thiosemicarbazones were in the ranges of 70—240 °C and 165—240 °C respectively.

Table 1. Response factors ($F_i$) and average deviations of thiosemicarbazones

| Thiosemicarbazone of | Mp (°C) | Dp (°C) | Analytical condition | $F_i$ value and average deviation |
|---|---|---|---|---|
| Acetaldehyde | 139—140 | 180—185 | a | 13.86±0.04 |
| Acetone | 185—186 | 190—195 | a | 13.73±0.09 |
| Propionic aldehyde | 144—146 | 196—200 | d | 13.90±0.00 |
| Methyl ethyl ketone | 103—104 | 201—205 | d | 13.26±0.04 |
| Diethyl ketone | 85— 86 | 185—190 | d | 12.83±0.04 |
| Methyl *n*-propyl ketone | 75— 76 | 200—204 | d | 13.70±0.00 |
| Crotonic aldehyde | 159—161 | 200—205 | d | 13.90±0.00 |
| Methyl *sec*-butyl ketone | 71— 72 | 200—205 | d | 13.90±0.00 |
| Methyl *n*-amyl ketone | 78— 79 | 200—205 | d | 13.40±0.00 |
| Acetophenone | 119—120 | 220—227 | a | 13.53±0.04 |
| Benzaldehyde | 151—152 | 237—240 | b | 14.06±0.04 |
| *p*-Tolualdehyde | 172—173 | 237—240 | c | 14.66±0.04 |
| *p*-Hydroxybenzaldehyde | 238—240 | 238—240 | c | 15.06±0.47 |

a) $N_2$ 20 ml/min, 150 °C isothermal. b) $N_2$ 30 ml/min, 200 °C isothermal. c) $N_2$ 30 ml/min, 150—200 °C (20 °C/min). d) $N_2$ 30 ml/min, 150 °C isothermal.

The reproducibility and the uniformity of the response for various carbonyl compounds were evaluated with the thiosemicarbazones of 3 aliphatic aldehydes, 6 aliphatic ketones, 3 aromatic aldehydes, and one aromatic ketone. As is shown in Table 1, the response factors of these thiosemicarbazones, except in formaldehyde and *p*-hydroxybenzaldehyde, had a great uniformity and a high reproducibility over a wide range of homologous series.

The poor uniformity in the responses for the thiosemicarbazones of formaldehyde and *p*-hydroxybenzaldehyde is associated with a thermal decomposition of the derivatives in the gas-chromatographic system, because these two thiosemicarbazones have the same melting points as decomposition points.

Table 2. Relative retention values of thiosemicarbazones

| Thiosemicarbazone of | Relative retention values | | |
|---|---|---|---|
| | A | B | C |
| Formaldehyde | — | 4.88 | — |
| Acetaldehyde | 2.96 | — | — |
| Acetone | 3.46 | — | — |
| Propionic aldehyde | 4.37 | — | — |
| Methyl ethyl ketone | 4.86 | — | — |
| Acrolein | 4.95 | — | — |
| Diethyl ketone | 7.16 | — | — |
| Methyl *n*-propyl ketone | 7.98 | — | — |
| Crotonic aldehyde | 9.84 | — | — |
| Methyl *sec*-butyl ketone | 10.14 | 6.19 | — |
| Methyl *n*-amyl ketone | 19.44 | 9.99 | — |
| Acetophenone | — | 12.21 | 2.50 |
| Benzaldehyde | — | — | 6.17 |
| *p*-Tolualdehyde | — | — | 7.50 |
| *p*-Hydroxybenzaldehyde | — | — | 22.00 |

A: $N_2$ 30 ml/min, 125 °C isothermal, inlet temp. 150 °C.
B: $N_2$ 30 ml/min, 160 °C isothermal, inlet temp. 160 °C.
C: $N_2$ 30 ml/min, 200 °C isothermal, inlet temp. 200 °C.

The determination of the relative retention values of 15 thiosemicarbazones under the analytical conditions listed in Table 2 indicated that, using a 4 mm i.d. × 1 m glass column packed with Diasolid ZT, the direct gas-chromatographic analysis of the carbonyl thiosemicarbazone offers the best potential for the clear separation of the individual carbonyl compound commonly encountered in auto mobile exhausts[10] or in concentrated air samples.

In the gas-chromatographic analysis of the carbonyl compounds *via* their thiosemicarbazones, utilizing the selective response of the detector (FPD) for the sulfur compounds, purification is not required and a crude sample containing impurities can be used directly as the analytical sample. However, in the case of the identification of the individual carbonyl compounds by GLC-Mass analysis, the carbonyl compound to be iden-

Table 3. Separation and regeneration of the carbonyl compounds *via* thiosemicarbazone/$AgNO_3$ complex

| Carbonyl compounds | Recovery (%) |
|---|---|
| Acetaldehyde | 65.2 |
| Diethyl ketone | 51.0 |
| Acetophenone | 48.8 |
| Crotonic aldehyde | 65.3 |
| Benzaldehyde | 44.8 |

tified must be isolated from any foreign compounds.

The method of the regeneration of the parent carbonyl compound by treating carbonyl DNPH with mineral or organic acid cannot be applied to the unsaturated carbonyl compound and aromatic aldehydes. Similarly, method of producing the corresponding carboxylic acid by ozonization of the carbonyl DNPH cannot be applied to the unsaturated compound.

In this study, the isolation and subsequent regeneration of the parent carbonyl compounds was carried out through a heavy metal complex of thiosemicarbazone. Thiosemicarbazone is known to form an insoluble metal complex with heavy metal salts, *e.g.*, silver nitrate, cupric acetate, mercuric acetate, and mercuric cyanide. The metal complex can be decomposed to regenerate the thiosemicarbazone by a reaction with hydrochloric acid or hydrogen sulfide, and the thiosemicarbazone can be hydrolyzed to regenerate the parent carbonyl compound by heating it with mineral acid. In this work, the regeneration of the carbonyl compound *via* the thiosemicarbazone silver nitrate complex was studied in an attempt to isolate the carbonyl compound from the contaminated air sample. Table 3 indicates that the regeneration of the parent carbonyl compound, even with unsaturated or aromatic aldehyde, can be done with a 45—65% recovery.

In the analysis of the carbonyl compound in automobile exhaust by the carbonyl DNPH method, the presence of $NO_x$ in the sample gas has been reported to interfere with the formation of the 2,4-DNPH derivative and the subsequent gas chromatographic analysis.[3)]

In this study, the effect of $NO_2$ on the preparation of thiosemicarbazone and the subsequent gas chromatographic analysis were examined with crotonic aldehyde, methyl ethyl ketone, and propionic aldehyde. In the presence of a 1/10 molar equivalent of $NO_2$, no evidence was found for the interference of $NO_2$ in the formation of thiosemicarbazones, which can be deduced by a comparison of the melting points of the crude and the purified products and by an examination of the gas chromatograms of the crude products.

In the presence of an equimolar amount of $NO_2$, although the saturated aldehyde and ketone were subject to no practical interaction with $NO_2$, an apparent interaction of $NO_2$ with the unsaturated aldehyde, crotonic aldehyde, was observed. The lower melting point of thiosemicarbazone and the appearance of foreign peaks in the gas chromatogram of the crude product indicated the occurrence of this side reaction.

## References

1) L. J. Papa and L. P. Turner, *J. Chromatogr. Sci.*, **10**, 744 (1972).
2) H. Kallio, R. Linko, and J. Kaitaranta, *J. Chromatogr.*, **65**, 355 (1972).
3) M. Fracchia, F. Schuette, and P. Mueller, *Environ. Sci. Tech.*, **1**, 915 (1967).
4) E. Fedeli and M. Cirimele, *J. Chromatogr.*, **15**, 435 (1964).
5) R. Soukup, R. Scarpellino, and E. Danielczik, *Anal. Chem.*, **36**, 2255 (1964).
6) M. W. Scoggins, *ibid.*, **45**, 2204 (1973).
7) J. W. Ralls, *ibid.*, **32**, 332 (1960).
8) M. Keeney, *ibid.*, **29**, 1489 (1957).
9) P. Ronkaiene and S. Brummer, *J. Chromatogr.*, **28**, 253 (1967).
10) D. Seizinger and B. Dimitriades, *J. Air Pollution Control Assoc.*, **22**, 47 (1972).
11) E. Campaigne, P. Monroe, B. Arnwine, and W. Archer, *J. Amer. Chem. Soc.*, **75**, 988 (1953).