# A COMPARISON OF SUPPORTS FOR QUANTITATIVE GAS CHROMATOGRAPHIC ANALYSIS OF NICKEL AND ZINC DITHIOCARBAMATES

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The gas chromatographic behaviour of nickel and zinc diethyldithiocarbamates was examined on various supports, mainly of the Chromaton and Chromosorb families, coated with polydimethylsiloxane nonpolar stationary phase. The coefficients of asymmetry, retention ratios and relative molar responses with respect to $C_{28}H_{58}$, and numbers of theoretical plates were determined. While poor results were obtained with Chromosorb G, Chromaton N Super appears to suit well to the determination.

The gas chromatography (GC) technique has recently been applied to the analysis of metal dialkyldithiocarbamates[1-6]. Tavlaridis and Neeb[4] were able to determine nickel diethyldithiocarbamate in quantities as small as 130 pg on a column packed with an inactive support (Chromosorb W PH) coated with a medium polar stationary phase (OV-25). The limit of determination could be lowered appreciably by analyzing metal perfluorodialkyldithiocarbamates using a selective electron capture detector.

The published data as well as our experience indicate that the results of GC analysis of metal dithiocarbamates are greatly influenced by the liquid phase support used. The aim of the present work therefore was to examine how the support coated with a nonpolar stationary liquid phase affects the quantitative analysis of nickel and zinc diethyldithiocarbamates.

## EXPERIMENTAL

The supports used were commercial products (Table I), the stationary phase was poly(dimethylsiloxane) OV-101 (Carlo Erba, Milan) applied in a 3% quantity with respect to the support mass. The glass columns used were 55 cm long, i.d. 3·5 mm.

The metal diethyldithiocarbamates were synthesized as described previously[1]. Fresh solutions were prepared for the analysis by dissolving the solids in distilled chloroform.

The packings were tested on a Fractovap 2300 chromatograph (Carlo Erba, Milan) equipped with a flame ionization detector. Nitrogen for lamps served as the carrier gas. The samples were injected with a 1 µl or 10 µl microsyringe. The peak areas were measured by means of an Autolab

6300 integrator (Spectraphysics, Darmstadt). One μl mixtures containing about 1 μg of nickel diethyldithiocarbamate (Ni(DEDTC)$_2$) and about 0·2 μg on n-octacosane ($C_{28}$) were analyzed at 230°C. Triplicate measurements were carried out in 45 min periods.

The relative molar response (R.M.R.) values were evaluated for Ni(DEDTC)$_2$ with respect to $C_{28}$ based on the peak areas per unit amounts of substance. The coefficients of asymmetry (*As*) were determined for Ni(DEDTC)$_2$ as $As = 100a/b$, where *a* and *b* are the widths measured at 10% peak height.

TABLE I

Characteristics of the supports tested

| Name | Grain size mesh | Manufacturer |
|---|---|---|
| Chromaton N Super | 90/120 | Lachema, Brno, Czechoslovakia |
| Chromaton N AW HMDS | 90/120 | Lachema, Brno, Czechoslovakia |
| Chromaton N AW DMCS | 90/120 | Lachema, Brno, Czechoslovakia |
| Inerton AW HMDS | 90/120 | Lachema, Brno, Czechoslovakia |
| Chromosorb W HP | 80/100 | Supelco, Bellefonte, USA |
| Chromosorb W (sil) | 80/100 | Carlo Erba, Milan, Italy |
| Chromosorb G DMCS | 80/100 | Becker, Delft, The Netherlands |
| Chromosorb G | 80/100 | Carlo, Erba, Milan, Italy |

TABLE II

Coefficients of asymmetry (*As*), retention ratios (*r*) and relative molar responses (R.M.R.) with respect to $C_{28}H_{58}$ and numbers of theoretical plates (*n*) for gas chromatographic treatment of nickel diethyldithiocarbamate on supports coated with 3H OV 101 stationary phase

| Support | *As* % | *r* | R.M.R. | *n* |
|---|---|---|---|---|
| Chromaton N Super | 100 | 1·49 | 0·182 | 450 |
| Chromaton N AW HMDS | 100 | 1·48 | 0·135 | 770 |
| Chromaton N AW DMCS | 100 | 1·50 | 0·181 | 430 |
| Inerton AW HMDS | 93 | 1·50 | 0·214 | 560 |
| Chromosorb W PH | 100 | 1·49 | 0·118 | 1 050 |
| Chromosorb W (sil) | 87 | 1·54 | 0·163 | 1 020 |
| Chromosorb G DMCS | 100 | 1·48 | 0·183 | 630 |
| Chromosorb G | 15 | 1·69 | 0·087 | 870 |

## RESULTS AND DISCUSSION

The coefficients of asymmetry, retention ratios, and the relative molar response averages of triplicate measurements, for the packings based on the supports of Table I, are given in Table II.

From the point of view of the peak asymmetry, as expressed by the coefficient of asymmetry, the Chromosorb W and, in particular, Chromosorb G supports coated with the nonpolar phase are not very convenient for a GC analysis of Ni.$(DEDTC)_2$. Also, the retention ratios for the two supports are apparently higher than for the remaining materials, thus indicating that in addition to the distribution mechanism, adsorption phenomena contribute to the retention on the packings in question.

The relative molar response values are not constant. The lowest value is again observed for Chromosorb G; so this support is apparently unsuitable for a quantitative GC analysis of $Ni(DEDTC)_2$. Rather surprising, however, are the low responses established for Chromaton NAW HMDS and Chromosorb W HP.

For a comparison of the efficiency of the various packings, the numbers of theoretical plates were calculated based on the peaks of $Ni(DEDTC)_2$ (Table II).

With respect to the complex of data given in Table II, Chromaton N Super coated with 3% OV-101 emerges as a suitable packing for the GC analysis of $Ni(DEDTC)_2$. The calibration plot for this system is shown in Fig. 1 (curve *1*). The technique enables 10 ng of $Ni(DEDTC)_2$ to be determined reliably. The data were subjected to the least squares treatment to give the regression straight line equation

$$y = 1{\cdot}65 + 18{\cdot}2x ,$$

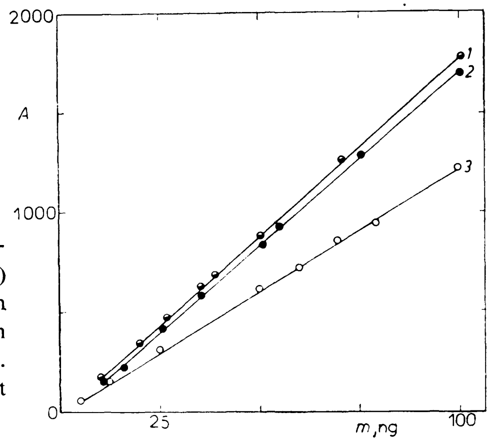

FIG. 1

Calibration plots for the gas chromatographic analysis of nickel (*1*, *2*) and zinc (*3*) diethyldithiocarbamates on columns with 3% OV-101 stationary phase on Chromaton N Super (*1*) and Chromosorb W PH (*2*, *3*). *A* peak area in digit units, *m* injected amount in ng where $y$ is the peak area in digit units and $x$ is the injected amount of $Ni(DEDTC)_2$ in ng.

The highest separating efficiency as expressed by the number of theoretical plates is attained with Chromosorb W PH (Table II). In view of the facts that this support is commonly used for the GC analysis of dithiocarbamates and that a high separating efficiency is frequently required, the calibration curve was plotted also for this support (Fig. 1, curve 2). The corresponding straight line equation is

$$y = 2{\cdot}19 + 12{\cdot}42x\,,$$

showing that while the error of determination is nearly the same as in the preceding case, the sensitivity (the slope of the straight line) is appreciably lower for Chromosorb W PH than for Chromaton N Super.

A considerably higher systematic error is obtained with Chromosorb W PH in the GC analysis of $Zn(DEDTC)_2$ (curve *3* in Fig. 1); the equation fitting the calibration graph is

$$y = -23{\cdot}26 + 17{\cdot}43x\,.$$

The calibration straight line equations can be handled to give the relative errors of determination of 10 ng of $Ni(DEDTC)_2$ on the supports coated with 3% OV-101, namely, −1% for Chromaton N Super and −2% for Chromosorb W PH; for 10 ng of $Zn(DEDTC)_2$ and the latter support the error is as high as +15%.

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