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Note

Liquid chromatography of dimethyldithiocarbamate degradation products

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High-performance liquid chromatographic (HPLC) analysis of metal complexes of N-disubstituted dithiocarbamic acids was described in previous papers[1–5]. That work confirmed that metal dithiocarbamates (DTC) are not stable and decompose very quickly.

Metal chelates of dithiocarbamic acids (especially methyl derivatives) are widely used in agriculture as active fungicides [ferbam, iron(III)dimethyldithiocarbamate; ziram, zinc dimethyldithiocarbamate]. As DTC complexes are known to have toxicological and mutational effects[6], it is necessary to have a rapid and accurate method for the separation, identification and determination of DTC chelates and their degradation productions.

The separation of the main degradation products in model mixtures and real samples has been achieved using gradient elution[7,8]. Many workers have demonstrated the relationship between the chemical structure and biological activity of various DTC complexes[9–11], and it has been confirmed that the degradation products of DTC chelates were more effective than the original complexes[12,13]. Fungicide activities have also been reported for homologous series of some dialkyldithiocarbamate complexes[14,15]. Some papers have dealt with the separation of metal DTC chelates using adsorption and reversed-phase chromatography[16–19]. The influence of UV radiation, temperature and oxidizing agents on the decomposition of ferbam and its determination in real samples was studied using thin-layer chromatography and HPLC[20].

The aim of this work was to establish the optimal conditions for the simultaneous HPLC separation of ferbam and its possible degradation products with the minimum separation time and with maximum resolution. Adsorption and reversed-phase chromatography were investigated and the results obtained were compared. The optimal separation conditions were used in HPLC studies of the ferbam heat decomposition process.

EXPERIMENTAL

Apparatus

All experiments were carried out on a Spectra-Physics Model 3500 commercial

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high-performance liquid chromatograph with a UV detector. For HPLC separations three metal columns (250 × 4.6 mm I.D.) were used: LiChrosorb Si-100 (particle diameter 5 μm), LiChrosorb Si-100 (particle diameter 7 μm) and LiChrosorb RP-18 (particle diameter 5 μm).

Three combinations of mobile phases were investigated: chloroform–cyclohexane and chloroform–*n*-hexane in adsorption chromatography and acetonitrile–methanol–water in reversed-phase chromatography.

An AEI 902 S mass spectrometer (7–70 eV, 0.1 mA, 323–375°K) was used.

Chemicals

All organic solvents were of analytical-reagent grade (Lachema, Brno, Czechoslovakia) and were dried over magnesium perchlorate and redistilled. Ferbam was synthesized according to the literature[8] and its purity was established by elemental analysis using a Model 1102 elemental analyser (Carlo Erba, Milan, Italy) and mass spectrometry. Solutions (0.001 *M*) of ferbam were injected using a 10-μl Hamilton syringe.

Procedure

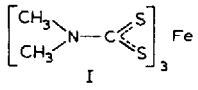
The samples were decomposed at 323, 348, 373, 398, 423 and 493°K.

RESULTS AND DISCUSSION

According to published results[7,21] the following scheme for the degradation of ferbam has been proposed:

Ferbam
↓
TMTD ↔ TMTM ↔ TMTU

where ferbam = iron(III) dimethyldithiocarbamate (I), TMTD = tetramethylthiuram disulphide (II), TMTM = tetramethylthiuram monosulphide (III) and TMTU = tetramethylthiourea (IV).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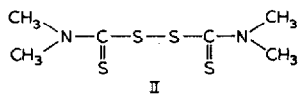
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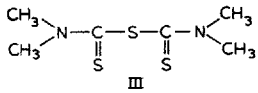
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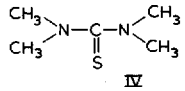
IV

In order to choose the optimal conditions for the HPLC separation of the degradation products of DTC complexes the resolution R_{ij}, was determined as the main criterion.

A column packed with LiChrosorb RP-18 was used for reversed-phase chromatography. Adsorption liquid chromatography was applied for the optimal separation of ferbam and its three degradation products. We investigated many mobile phases and chose chloroform (50–100%) in cyclohexane or *n*-hexane. Two main de-

TABLE I

N_R AND t_{Rn} VALUES FOR TMTM AND TMTU

Column: LiChrosorb Si-100, 5 μm (250 × 4.6 mm I.D.). Mobile phases: chloroform–cyclohexane and chloroform–*n*-hexane.

Mobile phase	N_R	t_{Rn} *(sec)*
$CHCl_3$–C_6H_{12} (80:20)	11,665	217.3
$CHCl_3$–C_6H_{12} (70:30)	9804	207.0
$CHCl_3$–C_6H_{12} (60:40)	9911	242.0
$CHCl_3$–C_6H_{12} (50:50)	12,739	348.7
$CHCl_3$–C_6H_{14} (70:30)	14,550	325.3
$CHCl_3$	18,338	339.6

mands on the choice of the separation system were the minimal number of theoretical plates, N_R, and the minimal time necessary for the separation of the last component, t_{Rn}[22].

It was obvious in adsorption chromatography that the largest value of N_R is

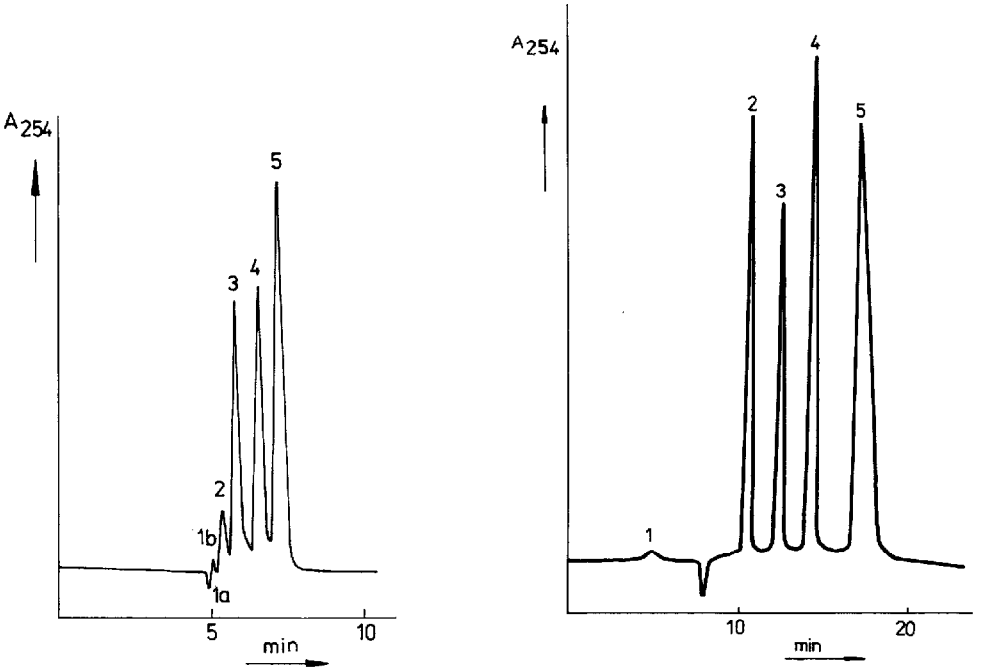

Fig. 1. Separation of ferbam and its degradation products using a LiChrosorb Si-100, 5 μm, column (250 × 4.6 mm I.D.). Mobile phase: chloroform–cyclohexane (70:30). Flow-rate: 0.6 cm^3/min. Pressure: 1.93 MPa. Peaks: 1, inert; 2, ferbam (k' = 0.13); 3, TMTD (k' = 0.26); 4, TMTM (k' = 0.40); 5, TMTU (k' = 0.62).

Fig. 2. Separation of ferbam and its degradation products using a LiChrosorb RP-18, 5 μm, column (250 × 4.6 mm I.D.). Mobile phase: acetonitrile–methanol–water (37:33:30). Flow-rate: 0.33 cm^3/min. Pressure: 15.9 MPa. Peaks: 1, inert; 2, TMTU (k' = 1.07); 3, TMTM (k' = 1.45); 4, TMTD (k' = 1.81); 5, ferbam (k' = 2.75).

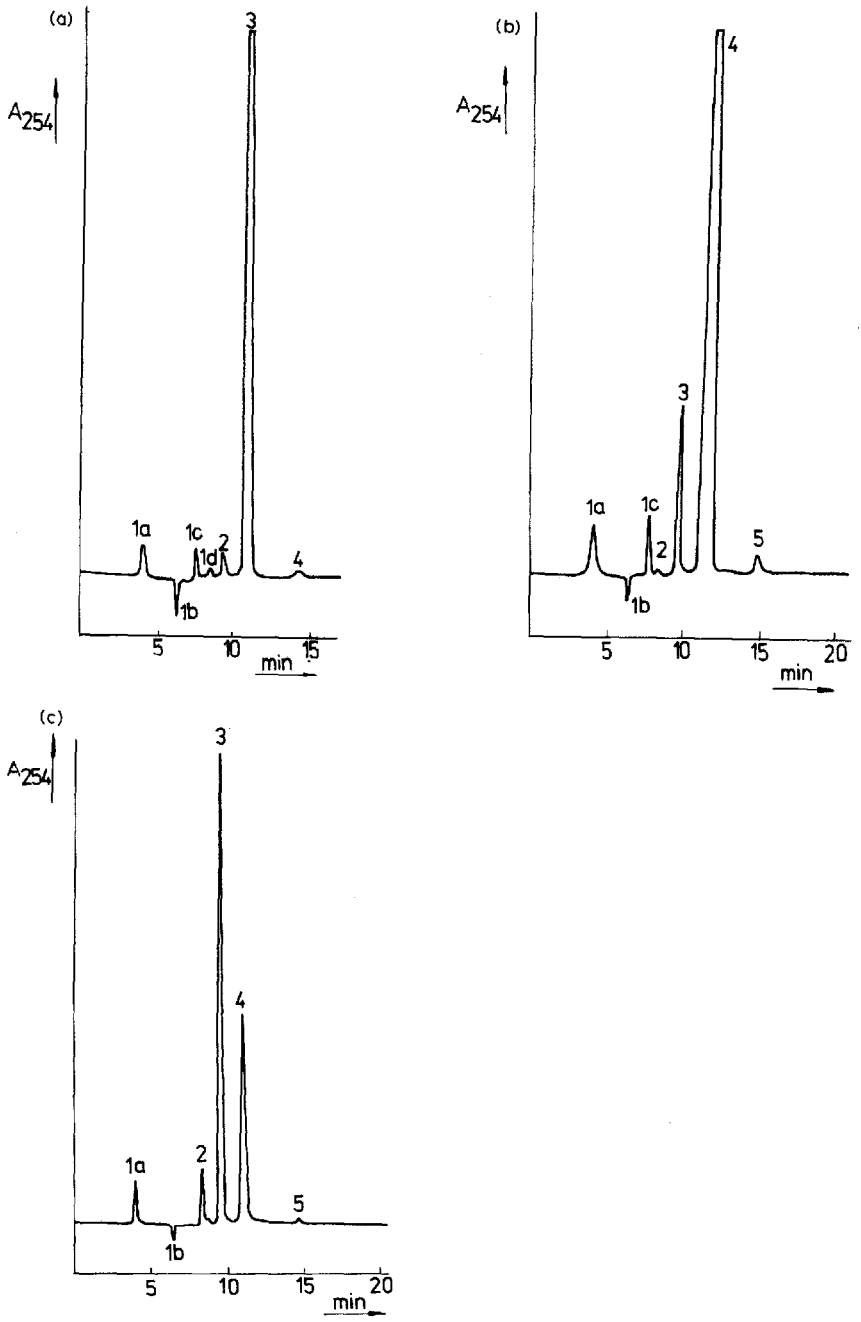

Fig. 3. Separation of ferbam heat degradation products using a LiChrosorb RP-18, 5 μm, column (250 × 4.6 mm I.D.). Mobile phase: acetonitrile–methanol–water (37:33:30). Flow-rate: 0.33 cm^3/min. Pressure: 15.9 MPa. (a) 323°K. Peaks: 1, inert; 2, TMTM; 3, TMTD; 4, ferbam. (b) 398°K. Peaks: 1, inert; 2, TMTU; 3, TMTM; 4, TMTD; 5, ferbam. (c) 423°K. Peaks: 1, inert; 2, TMTU; 3, TMTM; 4, TMTD; 5, ferbam.

necessary for the separation of TMTM and TMTU. Table I gives the N_R and t_{Rn} values for these components. On the basis of the results we chose as the optimal separation system chloroform–cyclohexane (70:30).

TABLE II

CONCENTRATIONS OF TMTU, TMTM, TMTD AND FERBAM AFTER HEATING

Temperature (°K)	*TMTU (%)*	*TMTM (%)*	*TMTD (%)*	*Ferbam (%)*
323	–	1.16	97.77	1.07
348	–	1.58	97.43	0.99
373	–	2.07	97.14	0.79
398	0.21	3.80	95.35	0.65
423	6.47	66.46	26.54	0.53

Reversed-phase liquid chromatography has also been used for the effective separation of DTC complexes and their degradation products[20]. In comparison with adsorption chromatography, the R_{ij} values were higher but the separation time was about three times higher.

Figs. 1 and 2 demonstrate the separation of ferbam and its degradation products using adsorption and reversed-phase chromatography.

The optimal separation criteria were for adsorption chromatography, $R_{\text{ferbam,TMTD}} = 1.08$, $R_{\text{TMTD,TMTM}} = 1.32$, $R_{\text{TMTM,TMTU}} = 1.40$ and time of analysis = 7 min, and for reversed-phase chromatography, $R_{\text{ferbam,TMTD}} = 2.32$, $R_{\text{TMTD,TMTM}} = 2.75$, $R_{\text{TMTM,TMTU}} = 3.81$ and time of analysis = 20 min.

The combination of reversed-phase HPLC and mass spectrometry was used for the study of the heat degradation process of ferbam. The samples of ferbam were dissolved in chloroform and methanol and the decomposition products were injected into the column. The mobile phase was acetonitrile–methanol–water (37:33:30).

Fig. 3 illustrates the chromatograms of ferbam heated at 323, 398 and 423°K. The contents of TMTU, TMTM and TMTD in ferbam after heating are given in Table II. At about 420°K most of the TMTD was converted into TMTM (418°K is the melting point of TMTD).

In conclusion, HPLC permits the rapid separation of less stable DTC complexes and their degradation products and has also been applied in trace analysis of residues of DTC complexes in real samples (soil, cucumber)[20]. The conditions for the separation of dibutyldithiocarbamates and their degradation products in model mixtures and in agricultural products will be reported later.

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