METAL-CHELATE GAS-CHROMATOGRAPHY FOR TRACE ELEMENT ANALYSIS

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Abstract - 1,1-dithiolato-chelates, especially dithiocarbamates,
have proved very useful in gas chromatographic analysis of
inorganic elements. Fluorination of diethyldithiocarbamates
markedly improves volatility and gaschromatographic behaviour.
With this reagent up to ten elements can be separated by gas-
chromatography. All compounds can easily be extracted from
aqueous solutions by organic solvents, thus allowing to take
full advantage of the facilities which extraction procedures
offer. By proper choice of gaschromatographic conditions,
determination of elements in solutions in the ppm and higher
ppb-range is possible.

Gas-chromatographic trace element analysis in aqueous solutions can be car-
ried out via quantitative reaction of these ions to form volatile and
thermally stable compounds. The derivatization technique mostly used is the
transfer of metal-ions into their chelate form with the formation of the
chelates being rapid and quantitative even in trace concentrations. A
further prerequisite for the adaptation of these techniques to problems
of applied trace element analysis is, that the product compounds can easily
be isolated. The preferentially used technique is liquid/liquid extraction,
resulting in a transfer of the formed chelate compounds from the aqueous
solutions into an organic phase thus combining separation of the trace
compounds with their enrichment in the organic phase. A large reaction range
of the ligand is necessary for multi-or oligoelement analysis in a single
step. Early investigations in chelate gas-chromatography were concerned
with the application of 1,3-diketones and their derivatives (1). However,
because of the slow and non-quantitative nature of the reactions of these
chelating agents in aqueous systems, their application in oligoelement trace
analysis is still comparatively small. Further developments in chelate gas-
chromatography are referred in (2). Most promising results have been
obtained by application of 1,1-dithiolato-chelates, yielding volatile,
thermally stable and extractable metal chelates with a large number of
elements in aqueous solutions, thus allowing oligo-elementanalysis by gas-
chromatography. Table 1 contains a survey of chelate systems known to date
suitable for trace element analysis by gas-chromatography after separation
by liquid liquid extraction.

TABLE 1. Survey of ligands for extractive chelate gas-chromatography
of elements

Ligand	Elements	References
4,4'(ethane-1,2 diyldiimino)-bis-(pent-3-en-one)	Zn, Cu, Ni	3
Bis(acetylpivalylmethane)-ethylenediimine	Cu, Ni	4
Hexafluoroacetone + di-n-butylsulphoxide	Zn	5
Dialkyldithiophosphate	Ni, Zn, Pd, Pt	6,7
Diethyldithiophosphinate	Cd, Pb, Zn	8,9

Dialkyldithiophosphinate	Zn, Ni, Co, Pb, Cu	10
Diethyldithiocarbamate	Ni, Cu, Zn, Cd, Co, Pb, Pd, As, Rh, Se, Pt	11, 18, 19, 20, 21, 22, 23
Dialkydithiocarbamate	Ni, Cu, Pb, Cd, Zn	16 - 22
Ditrifluorethyldithio- carbamate	Zn, Cd, Cu, Ni, Co, Hg, Pb, Bi, Fe, Pt, Pd, Rh, Sb, Tl, In, Cr, Se	11 - 15

Some results of our investigations on substituted dithiocarbamates and di-
thiophosphinates will be discussed further. In the case of dithiocarbamates
an especially striking feature of these compounds is that fluorination
leads to high increase in volatility with unchanged thermal stability as
Fig. 1 shows for the Ni-diethyldithiocarbamate and the Ni-bis(trifluor-
ethyl-dithiocarbamate. A rise in vapor pressure of the order of more than
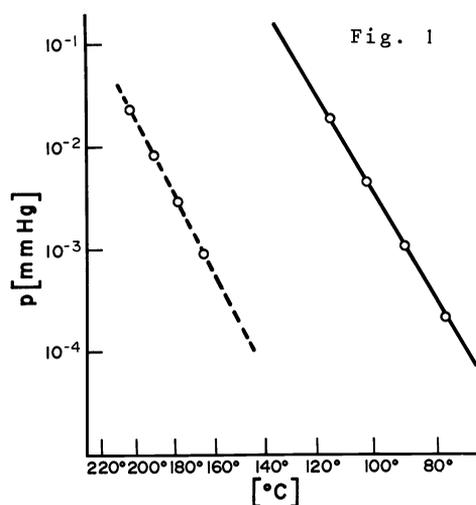two decades occurs, the same holds for the other metal-chelates of this
ligand (24).

Fig. 1. Vapor pressure of fluorinated (————) and unfluorinated
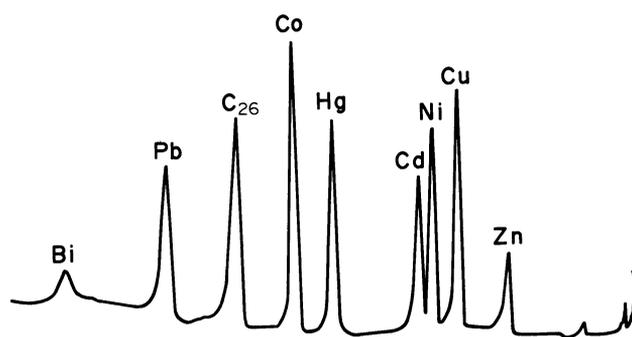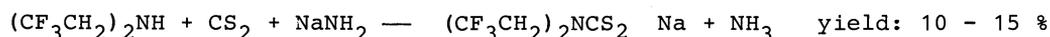(------) Ni-bis(diethyldithiocarbamate). C.f. (24).

Fig. 2. Gaschromatogram of a mixture of trifluorethyldithiocarbamates.
Automatic sampler with quartz column and quartz capillaries (see text).
Amount of chelate: 0.1 µg/2.3 µl $CHCl_3$. GC-conditions: OV 25, 3 % on
chromosorb W-HP, 900 x 2 mm, 120-210°, 2°/min, FID-N_2.
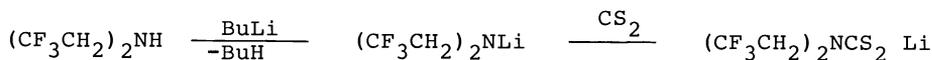
Higher fluorination, as for instance in the pentafluorpropyl-compound, yields
a still higher volatility whereas the heptafluorobutylligand forms chelates
with properties similar to those of   the trifluorethylligand (25). Low
yield in the preparation of these chelate-forming reagents has prevented
them from being used widely in trace element gas-chromatography. For the
time being the trifluorethyldithiocarbamate seems to be one of the most
powerful reagents in the determination of trace elements by chelate gas
chromatography.

The ligand can be synthesised in three ways:

1. reaction of secondary amines in presence of sodamide with carbondisulfide.
   Usual reaction for the preparation of substituted dithiocarbamates, low
   yield with bis(trifluorethyl)amine
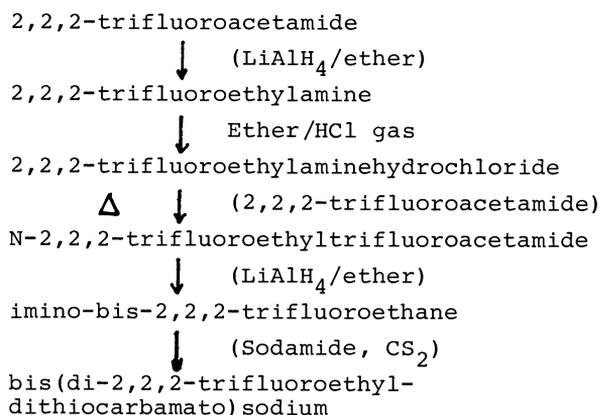
   $(CF_3CH_2)_2NH + CS_2 + NaNH_2$ —— $(CF_3CH_2)_2NCS_2$ Na + NH_3 yield: 10 - 15 %

2. reaction of bis(trifluorethyl)amine, n-butyllithium and carbondisulfide
   leading to lithiumdi(trifluoroethyl)dithiocarbamate salt (26):

$$(CF_3CH_2)_2NH \quad \xrightarrow[\text{-BuH}]{\text{BuLi}} \quad (CF_3CH_2)_2NLi \quad \xrightarrow{\text{CS}_2} \quad (CF_3CH_2)_2NCS_2 \, Li$$

<div align="right">yield: 65 %</div>

3. reaction according to the following scheme (27):

2,2,2-trifluoroacetamide

↓ (LiAlH$_4$/ether)

2,2,2-trifluoroethylamine

↓ Ether/HCl gas

2,2,2-trifluoroethylaminehydrochloride

Δ ↓ (2,2,2-trifluoroacetamide)

N-2,2,2-trifluoroethyltrifluoroacetamide

↓ (LiAlH$_4$/ether)

imino-bis-2,2,2-trifluoroethane

↓ (Sodamide, CS$_2$)

bis(di-2,2,2-trifluoroethyl-
dithiocarbamato)sodium

In spite of low yields, the procedure is interesting due to the inexpensive
and easily availble starting material, trifluoracetamide.

Compared with the unfluorinated diethyldithiocarbamate, the stability constant
of the sodium salt, dependent on pH, is shifted at lower pH by two orders
of magnitude, thus allowing to perform reactions in more acid solutions (28).
For the same reason the distribution of the free acid between organic phase
and aqueous solution is also shifted toward lower pH; reaction width and
extraction behaviour of the trifluorethydithiocarbamates are similar to those
of the diethyldithiocarbamates. According to present knowledge the following
ions give extractable species for gaschromatographic determinations:
Cr, Zn, Cd, Pb, Sb, Bi, Ni, Co, In, Tl, Fe, Hg, Pd, Pt, Rh, Se.

The gaschromatographic separation of up to ten elements is possible even with
packed columns (see Fig. 2).
To obtain the gas-chromatogram of Fig. 2 an automatic sampler, type 952
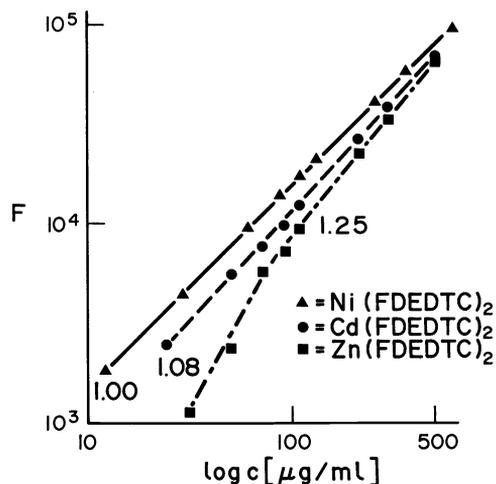Carlo Erba, was used in the following way (29):

Fig. 3. Calibration curves of Ni-, Cd- and Zn-bis(trifluorethyl-
dithiocarbamates (c.f. (36)).
GC-conditions: OV 210, 10 % on chromosorb WHP, 900 x 2 mm,
135 - 185°, 2°/min, FID-N$_2$. Injection volume: 1 µl CHCl$_3$.

The sample solution, 2.3 µl, is drawn up by glass or quartz capillaries of
6 mm length and 0.7 mm bore. After evaporation of the solvent in a protec-
ting Al-block adjacent to the injection port, the capillaries are directly
inserted into the injector. This way of dosaging offers several advantages,
f.i. use of larger sample volumes by repetition of filling, elimination of
solvent peak and free choice of solvent in connection with an ECD (halogena-
ted solvents can be used).

As is common in gas-chromatography with compounds containing hetero-
atoms, selectivity and sensitivity can be increased by use of special
detectors. In the case of diethyldithiocarbamates the use of N-sensitive
TID has considerably increased the sensitivity of determination with
better separation or even supression of the solvent peak (16). With an
ECD and the trifluorethyldithiocarbamates, a mixture of the Ni and Co
chelates can be determined on a packed column in the pg-region (12).

A general problem in chelate-gas-chromatography is the occurrence of decom-
position phenomena on columns and interactions with column fillings and
material (30-35), which are also observable with other polar substances.
This leads to non-linear calibration curves with low sample amounts.
These effects depend on the nature of the compound and the nature of the
column. So f.i. in a series of determinations of the Ni-, Cd- and Zn-bis-
(trifluorethyl)dithiocarbamates, see Figure 3, only the Zn-compound gives
a clearly non linear calibration curve in a bilogarithmic plotting with
slopes other than one. As we could observe, the nature of the support is
of extreme importance. In the determination of fluorinated Ni-chelates,
which, as we have seen, offer much less difficulties compared to the Zn-
compound, from a number of supports like Chromosorb 750, Chromosorb W-NAW,
Chromosorb W-AW-DMCS, Chromosorb W-HP and Gas Chrom Q, only the latter one
gave linear calibration curves between 5 and 1000 ng of chelate injected,
independent on the nature of the stationary phase (here OV 25, OV 101,
OV 210, GE SE 52) (38). Sometimes silanization, effective by deactivation
of active sites on the column, leads to a better linearity with "bad" or
even unsuitable columns but is in most cases without any significant
effect.

By the use of radioactively marked metal-chelates, interesting results have
been obtained as to where decomposition occurs in the column (31). With
a radioactive ^{65}Zn-trifluorethyldithiocarbamate-chelate, we found (37),
that most losses occur at the beginning and at the end of the column. At
that time we used columns with small plugs of glass wool as generally used
in gas-chromatography to prevent whirling up and losses of the support
material. Just at this place in the column, where the plugs were located,
a sharp rise in activity was observed. This is also the case with other
plug materials f.i. teflon and quartz wool. In fact when substituting wool
plugs by a small and thin metal gauze, a considerable improvement in gas-
chromatographic behaviour is observed with simultaneous improvements in
the linearity of the calibration curves (37). Additional improvement may
be obtained by the use of quartz-columns instead of glass columns. One
can state that the gas chromatography of small amounts of metal-chelates
is, in principle, possible by the proper choice of column composition and
column construction. Sometimes additional silanization improves the results.
The column effects observed with volatile chelates are in no correlation
with thermal stability data. In contrast they seem to be connected with
thermodynamical stability as f.i. Zinc is the most critical element and
Zn-chelates are known (in the 1st row of transition elements) to give the
most labile chelates according to the Irving-Williams rule. For the use of
metal-chelate-gas chromatography in practical trace element analysis,
extraction is a necessary prechromatographic step. For the practical work
special separating funnels connected with small vessels to collect the
organic phase are used (13). So the metals may be extracted from a
relatively large volume, f.i. 100 - 1000 ml. After the extraction step
the entire metal is obtained in 1 - 10 ml of the organic phase. It is
possible to evaporate the organic phase carefully to smaller volumes or
even to dryness and to take up the residue with a definite small volume
of an organic solvent, f.i. 50 µl. This procedure leads to a further
increase in sensitivity by the factor of 20, thus yielding a total
enrichment factor fo 1000 - 10 000. For quantitative evaluation a
constant amount of an inter. standard is added with the final addition
of organic phase. Mostly used inter. standards are the higher hydrocarbons.
Quantitative data are obtained by evaluating the peak area ratio of
chelate/internal standard and plotting it against concentration.

By use of the described procedure, the following simultaneous determinations of cations in aqueous solutions by chelate-GC with packed columns have been performed: 0.01 - 0.1 ppm Zn, Cd and Ni as diisopropyldithiocarbamates (17), 0.02 - 3 ppm Cd in presence of a large amount of Zn as diethyl-dithiophosphinate (9) and as trifluorethyldithiocarbamates: 0.2 - 3 ppm Bi and Pb (13), 5 - 1000 ppb Ni and Co (38), and down to 0.005 ppm Cr(III) and Cr(VI) (14).

Investigations have been made with capillary columns to improve sensitivity and separation of peaks (12,21,39,40). As mentioned above, decomposition processes are also limiting factors in chelate-GC with capillary columns, especially with thermodynamically unstable compounds like Zn-chelates. Our investigations with WCOT and SCOT columns and with various stationary phases have shown the superiority of WCOT-columns in chelate GC. Among the tested phases, GE SE 54, OV 17, and OV 101 gave comparable results. As in capillary chelate GC sensitivity is enhanced, the determination of extracted species is possible at lower levels with a good accuracy of retention values and peak area ratios (41). Figure 4 shows, for example, the determination of metals in aqueous solutions with sodiumditrifluor-ethyldithiocarbamate: After addition of 50 mg of pure sodiumchloride to 1000 ml untreated water, f.i. drinking water, a preextraction with 5 ml pure dichlormethane has been performed to remove organic extractable impurities. Then, after addition of 10 mg of the reagent, a further extraction is made with 10 ml dichlormethane containing 10 µg C_{18}/ml as inter.standard. After evaporation of the organic layer down to about 1 ml, 2 µl of the organic phase were injected using splitless injection. The method has proved useful for the determination of heavy metal contaminants in water (41), allowing f.i. the determination of Ni below 1 ppb.

Capillary gas chromatography of metal chelates seems to be a promising technique of growing importance in the near future. Taking advantage of the sophisticated developments like on-column injection and fused silica columns, remarkable improvements can be obtained even with elements yielding only bad chelates. So, for instance, in preliminary tests using a 30 m SE-52 fused silica column with on-column injection, temperature programme and an FID, gas chromatograms of Zn-trifluorethyldithiocarbamate (-----) could be obtained at levels of 5 ng chelate per 1.5 µl CCl_4, which is equivalent to 0.6 ng of Zn.
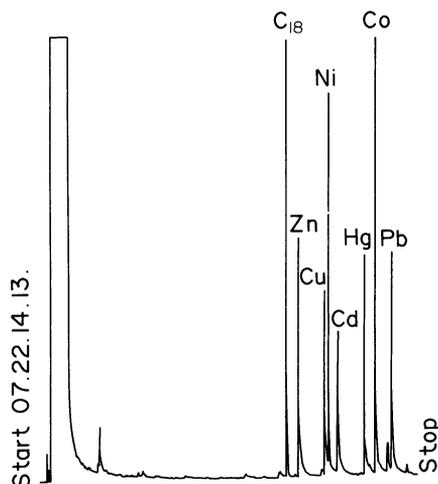

Fig. 4. Capillary gas-chromatogram of trifluorethyldithio-carbamates after extraction from aqueous solutions (see text). Metal contents of aqueous solution: Zn, Cu, Ni, Co-5 ppb, Cd-10 ppb, Hg, Pb-20 ppb.
GC-conditions: 20 m SE 54, 70 - 240°, 8°/min, 2 µl splitless injection, FID-He. C.f. (41).

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