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LIQUID CHROMATOGRAPHY–SPECTROMETRY WITH THE BUFFER-MEMORY TECHNIQUE

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SUMMARY

The utility of the buffer-memory technique in quantitative detection of liquid chromatographic (LC) effluents is demonstrated. Sub-microgram detection limits appear feasible for non-volatile compounds. A comparison of the buffer-memory technique and conventional liquid chromatographic–infrared spectroscopic (LC–IR) technique is made. Samples deposited on a KBr plate with the buffer-memory technique can be directly used to obtain more information. In particular, the chromatograms obtained by IR and X-ray fluorescence spectroscopy can be helpful in predicting the bonding between organic ligands and metals. This is demonstrated by introducing organotransition-metal complexes into the LC columns.

INTRODUCTION

With improvements in packing materials and pumps, high-performance liquid chromatography (LC) has become an extremely powerful technique for separating mixtures into their components. LC permits separations of a wide variety of mixtures containing non-volatile or thermally unstable compounds which can not readily be separated by gas chromatography (GC). However, no universal LC equipment equivalent to the thermal conductivity or flame ionization detector in GC is available, because various mobile phases are used and the physical properties of the mobile phase and sample components are often quite similar. The two detectors which have the widest range of applications are based on UV absorption and refractive index. However, these detectors provide little information other than retention time and fractional distribution.

The coupling of LC with mass spectrometry (LC–MS) has provoked considerable interest because of its capability for highly sensitive identification of components separated by LC. Several types of interface for LC–MS have been developed, but at present they are still far from being suitable for routine use.

Infrared (IR) absorption can be used for selective or universal detection in LC. Many efforts have been made to combine LC with IR spectroscopy on-line. These have involved two approaches, the direct flow cell technique and the automated diffuse reflectance–solvent elimination technique. Both approaches have some intrin-

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sic problems as described below, although they have been successfully applied to complex mixtures.

Recently, micro column LC, pioneered by Ishii *et al.*[1], has been gaining in popularity. Small column diameters (less than 1 mm) and flow-rates (of the order of microlitres per minute) are characteristics of this technique[2,3]. Very small samples compared with conventional LC are required and very high sensitivity can be achieved, because dilution within the column is reduced, concentration remains high and plate heights of 2–3 times the packing particle diameter are attainable. Consequently, deposition of the total effluent on suitable materials followed by spectrometric investigation is a very promising route to LC–IR, LC–luminescence, LC–MS, etc.[4].

We have proposed a new approach for LC–IR, namely the buffer-memory technique[5–10], in which micro column LC is employed for separation and a KBr plate was used as a transport medium to accept the total column effluent. The methodology utilized may be considered similar to that in the automated diffuse reflectance–solvent elimination technique, but there are some key differences. One of the major features of the buffer-memory technique is that a completely continuous IR chromatogram is obtained, free of interference from the mobile phase. The utilization of this technique is not limited to IR spectrometry. The sample deposited on the plate can be used again for analysis *in situ* by other diagnostic chemical techniques such as X-ray fluorescence (XRF), since the buffer-memory retains information concerning the sample in the form of a completely continuous *chromatogram.*

Our previous papers[5–10] were concerned with qualitative discussion of the buffer-memory technique as a means of IR detection of LC effluent. Here the technique is discussed quantitatively, and a brief comparison is made with conventional LC–IR. Further, the utility and facility are demonstrated for LC–XRF and MS identification.

Previous studies on LC–IR

Undoubtedly, direct flow cell IR detection offers benefits in simplicity and quantitation. A few studies employing filter or dispersive IR spectrometers for this purpose have been reported[11–14], but have dealt exclusively with size-exclusion chromatographic separations. The use of this type of IR detector is limited to mobile phases that are transparent (at least 30% transmission) at the wavelength of interest with a given cell pathlength. Unfortunately, most practical LC solvents have strong absorption bands in the mid-IR region so that some spectral regions are opaque. For qualitative identification, the flow must be stopped during elution of the peak of interest in order to scan through the wide frequency range of IR.

Fourier transform infrared (FT-IR) spectrometers offer many unique advantages over dispersive IR spectrometers. Most important for the flow cell detection of LC effluent is its rapid scan rate for large spectral regions, permitting the monitoring of numerous wavelengths during a single chromatographic run. In the last few years, LC has been interfaced with FT-IR in a flow-through configuration[15–20]. The column effluent is directed through a flow cell, and interferograms are measured successively and stored during the entire chromatographic run. The absorption bands due to the solvent system are then subtracted from the solute spectra. In favourable situations, a detection limit of about 100 ng for a typical solute can be obtained with a data aquisition time of 2–4 sec.

However, it is to be noted that the criteria for flow cell thickness selection are similar in spite of characteristic differences between dispersive and interferometric IR spectrometers. There is no optimum pathlength for all wavenumbers, so a compromise giving maximum cell thickness consistent with solvent transmission over all bands of interest must be determined experimentally[17–20]. When gradient elution is needed for the best separation, subtractive methods become extremely cumbersome.

An alternative is to collect the column effluent as a number of fractions using a special sampling technique, followed by solvent evaporation and IR measurements.

Griffiths and co-workers[21–23] have linked the solvent removal technique to interferometric IR spectrometry. In this case, the effluent from the UV detector of the chromatograph is first concentrated via a heated tube and then dropped onto a cup, containing powdered KCl, which is held in a carousel. After deposition, the carousel is rotated and the remaining solvent is eliminated during the time it takes for the following LC peak to be collected. The diffuse reflectance IR spectrum of the solute is then measured. Such a process is controlled by a minicomputer and repeated for all subsequent peaks. This technique enables one to circumvent the fundamental problems of the flow cell technique, caused by the presence of the mobile phase.

Nevertheless there are still a few difficulties. The interface needs a trigger actuated by the signal from the UV detector. Obviously, the components which have no absorption in the UV region cannot be conveniently handled with the system. In addition, since a small fraction of the peak exceeding a present threshold level is collected onto the cup; the possibility exists that minor components in the sample will be overlooked. Even if the effluent may be finely fractionated, the resulting IR chromatogram is essentially discontinuous. When the diffuse reflectance spectrum is plotted as the Kubelka–Munk function, the spectrum resembles an absorbance spectrum. The bandwidths as well as the relative intensities, however, can change considerably with the particle size[24]. Most of the spectra that have so far been published were measured by the transmission method. Therefore, if identification of the solute introduced into the system is to be accomplished by means of comparison with reference spectra, simple inspection of spectra may not be sufficient. This is particularly evident when the "observed" spectrum is compared with digitized library spectra stored in the IR instrument[25].

EXPERIMENTAL

In the buffer-memory technique, the effluent from the micro LC column is deposited onto a KBr crystal plate as a continuous, narrow band (width about 1–1.5 mm) with instantaneous evaporation of the mobile phase, using a specially made interface. After collecting all the solutes, the loaded plate, or "buffer-memory", is automatically brought into the optical path of a FT-IR spectrometer and interferometric data are successively collected as the memory traverses the beam. With a dispersive IR spectrometer, the peak of interest is located by finding the point of maximum IR absorbance (or minimum transmittance) at several IR frequencies and then the IR spectrum is scanned. Further details are given elsewhere[6].

Chromatography

The pumping system was a Jasco Familic 100N (Jasco,Tokyo, Japan). Sep-

arations were achieved by using a Jasco SS-05 (porous silica, 5 μm) packing material in PTFE tubing (10 cm × 0.5 mm I.D.) at a flow-rate of either 5 or 8 μl/min. Chromatographic grade solvents were used as received.

The sample size must be reduced in proportion to the column size and the column capacity. The amount of sample employed in a micro column of 0.5 mm I.D. is typically 5 μg or less without serious degradation of column efficiency[3]. In this work, samples of 1–6 μg were introduced and therefore the micro column LC system was not optimized for high-performance separation.

IR spectroscopy

IR measurements were performed on a Jasco A-3 grating infrared spectrometer and a JIR-40X Fourier transform infrared spectrometer (JEOL, Tokyo, Japan) equipped with a 15-bit analogue-to-digital converter and a mercury-cadmium-telluride (MCT) detector. The Jasco A-3 was set to scan at *ca.* 140 cm^{-1}/min (nominal resolution 8 cm^{-1}), using a five-fold gain. FT-IR spectra were measured at a resolution of 8 cm^{-1}. Each sample interferogram (50 scans co-added) was transformed by double precision (32 bit per word) software and ratioed against a stored spectrum of a slightly moist KBr surface.

A 3X beam condenser (Jasco BC-1) and a reference beam attenuator (Jasco AT-50) were necessary for all IR measurements.

X-Ray fluorescence spectrometry

X-Ray spectra were obtained with a Rigaku-Kevex 7000 X-ray fluorescence spectrometer system, consisting of a tungsten anode X-ray tube, a secondary target and filter assembly to provide irradiation facilities with Ge, Gd, Si, Ag and Ti *K*-radiation, a 30 mm^2 × 3 mm Si(Li) detector (170-eV resolution for Mn K_α at 5.895 keV), associated electronics for signal processing and a 2 × 1024-channel pulse height analyzer for data aquisition. Incident and detected radiations are collimated so as to obtain angles of *ca.* 45° with the sample plane for both. In this work the tungsten tube was operated at 40 kV, 25 mA and Ge was used as a secondary target.

Mass spectrometry

The mass spectra were measured with an EMD-05A (ESCO, Tokyo, Japan) equipped with electron impact ion source at a resolution $M/\Delta M \approx 350$, where $M+\Delta M$ are the mass numbers of two neighbouring peaks of equal intensity in the mass spectrum. The temperatures of the ion source and sample probe were 250°C and 230°C, respectively. The accelerating voltage was kept at 0.7 kV, the electron voltage at 70 V and the total electron emission current at 20 μA.

Materials

Di-*n*-propyl ketone 2,4-dinitrophenylhydrazone and N,N-diethyldithiocarbamates of chromium and cobalt were synthesized by standard methods. Copper N,N-diethyldithiocarbamate was purchased from Kanto Chemicals (Tokyo, Japan). A crystal of potassium bromide (width 35 mm, length 35 mm, thickness 3 mm) was obtained from Jasco. It was cut into four pieces (each *ca.* 8.8 mm in width and 35 mm in length) with a clean stainless-steel blade and used as a buffer-memory substrate.

RESULTS AND DISCUSSION

Quantitation

For quantitative purposes it is important to examine the applicability of Beer's law. Solutions containing measured amounts of di-*n*-propyl ketone 2,4-dinitrophenylhydrazone (each 1,3,4 or 6 μg) were successively introduced into the column and subsequently deposited onto a KBr plate, as described above. The FT-IR chromatograms derived from the buffer-memory are shown in Fig. 1. A unique advantage of this technique is that the IR chromatogram can be measured over a fairly wide frequency region because of thorough elimination of the mobile phase. Least squares analysis of the relative peak heights of the chromatograms against sample weight indicated that the data over a wide region (1600–1000 cm^{-1}) fit a straight line with a residual variance of $5.33 \cdot 10^{-4}$ in relative peak height units and that for the data at 1255 cm^{-1} the residual variance is $1.77 \cdot 10^{-2}$. A baseline was obtained for each peak by visually estimating the points which the peak ended. The larger deviation from linearity for the data at 1255 cm^{-1} can be attributed to ambiguity in the choice of baseline, which is caused by a large amount of baseline noise and drift. The magnitude of the baseline noise can determine the detection limit of this technique. As a rule of thumb, the present detection limit for the compounds seems to be less than 100 ng (*ca.* $4.5 \cdot 10^{-10}$ mol). This detection limit was obtained in spite of disparity between the IR beam size and the area upon which the sample was deposited. In fact, the size of the beam focus of the FT-IR spectrometer equipped with the 3X beam condenser was about 3.3 × 8 mm while that of the deposited solute band was spread over 2 mm, with a width of 1 mm. In order to minimize the noise from the clean area of the memorized plate, a small aperture (4 × 1 mm) was placed in front of the plate. Hence the measurement efficiency was reduced by a factor of about 20. It thus seems that matching of these parameters would result in an improvement of detection limit.

Another important aspect of quantitative detection by the buffer-memory technique is the reproducibility of the deposition, and of subsequent absorbance measurements. The reproducibility of the chromatogram is illustrated in Fig. 2. The relative standard deviation of the peak height was 6% for five different deposits of 2 μg of di-*n*-propyl ketone 2,4-dinitrophenylhydrazone.

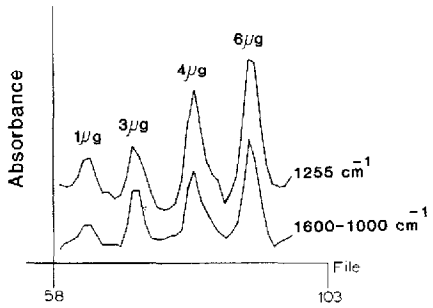


Fig. 1. Dependence of peak height of IR chromatogram on amount of sample. Solutions containing di-*n*-propyl ketone 2,4-dinitrophenylhydrazone were successively injected into a SS-05 column and eluted with *n*-hexane-dichloromethane (65:35) at 5 μl/min. The JIR-40X spectrometer was used.

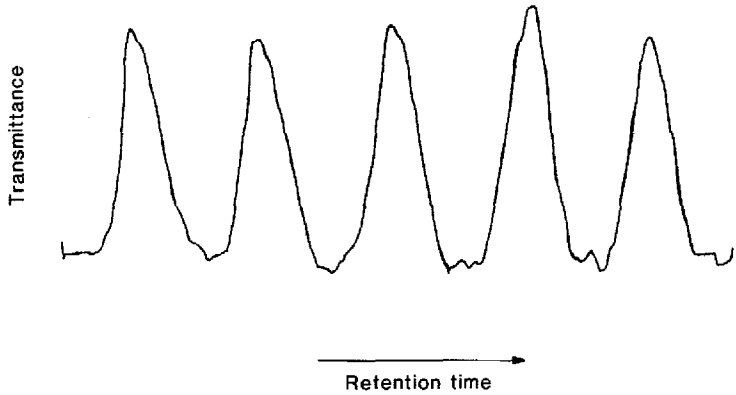


Fig. 2. IR transmittance chromatograms illustrating the reproducibility of the buffer-memory technique. Solutions containing 2 μg of di-*n*-propyl ketone 2,4-dinitrophenylhydrazone were successively injected. LC conditions as in Fig. 1. The measurements were made with the A-3 spectrometer, at 1265 cm^{-1}.

One might intuitively surmise that quantitative detection by the buffer-memory technique will be difficult, because there is the risk of adherence of the solutes to the stainless-steel capillary connecting tube. It is more important that each sample constituent is deposited in the same fraction, rather than that it is *totally* deposited. The results presented in Figs. 1 and 2 imply that we need not worry about this.

Comparison of LC–IR techniques

Vidrine[20] listed several characteristics required for LC–IR. Some of these are (a) high sensitivity, (b) applicability to all samples, (c) compatibility with all chromatographic solvents and (d) real-time chromatographic output.

In any LC–IR technique the sensitivity is a function of a number of factors including the absorptivity of the analyte, the chromatographic peak shape of the analyte, the presence or absence of interfering LC peaks and the type of IR instrumentation, the scan time and resolution used. With a 0.2-mm flow cell (internal volume 1.5 μl),Vidrine and Mattson[17] obtained a detection limit of the order of 100 ng in the beam path for a typical size-exclusion separation. However, the detection limit depended largely on the chromatographic peak volume and the cell thickness, and the presence of 100 ng of a substance in the beam path required a nominal injection of *ca.* 30 μg into the chromatograph. On the other hand, Kuehl and Griffiths[23] have demonstrated that the automated diffuse reflectance–solvent removal technique is capable of detecting sub-microgram quantities of a substance. However, that technique seems to be limited by difficulties in obtaining the chromatogram, as mentioned earlier.

Although the sensitivity of the buffer-memory technique was not optimized, the technique is capable of detecting amounts as low as 100 ng, as anticipated from Fig. 1. The deposition rate and the sample concentration significantly affect the attainable sensitivity. Moreover, this technique allows the chromatogram to be measured over a fairly wide frequency region (see Fig. 1), unlike the flow cell LC–IR technique. Whether or not the procedure is a definitive way to obtain highly sensitive detection, the apparent sensitivity should be enhanced.

Sample suitability is also an important factor for designing a practical LC–IR combination. The majority of samples used in our experiments were less volatile than the mobile phase. Some solutes separated by LC are highly volatile, so that loss of sample in the buffer-memory technique could occur through the sample deposition step. This situation also exists in the automated diffuse reflectance–solvent removal technique. However, this is not a serious problem because such solutes are conveniently separated by GC. Of course, the solutes may be thermally unstable and therefore cannot be separated by GC. In the buffer-memory technique the solutes are exposed to a moderate temperature (about 32°C) when using *n*-hexane–dichloromethane (65:35) as mobile phase. This temperature would have no harmful effects on most compounds. In contrast, the use of a flow cell promises non-destructive detection of LC effluents.

The problems caused by the presence of the liquid mobile phase are most serious in flow cell detection, as mentioned earlier. If complete spectra are described, high sensitivity can be traded for more complete spectral coverage by selecting a smaller cell thickness. Although spectral subtraction techniques are available with the existing commercial FT-IR spectrometers, they are not powerful enough to enable all solvent bands to be eliminated from the effluent spectra; solvent programming elution, in particular, causes difficult problems of solvent compensation. Such obstacles are not encountered in the LC–IR techniques utilizing solvent elimination. However, no technique has succeeded in detecting samples separated using aqueous mobile phases. The presence of water in the mobile phase prevented measurements of reasonable spectra in the flow cell configuration[26,27], and also removal of the mobile phase.

Only the flow cell detection technique meets the final requirement, that is, possesses the capability for real-time analysis.

An additional feature of the buffer-memory technique is that the effluent is deposited onto a piece of KBr crystal plate in the form of a chromatogram. Therefore, it is fairly easy to preserve the solutes for subsequent detailed characterization, in comparison with the automated diffuse reflectance–solvent removal technique.

Spectrometric identification with buffer-memory technique

The buffer-memory technique can be conveniently employed for sequential analysis of chromatographically separated organic and organically bound metal species by some spectrometric methods. In particular, *in situ* measurements by IR and XRF spectrometry enables one to obtain information on the bonding between organic molecules and metal elements. Fig. 3 illustrates the utilization of the proposed technique for structural elucidation of unknown analytes. It is noteworthy that the scheme proceeds from being non-destructive toward destructive.

Separation and IR detection (LC–IR). To demonstrate the feasibility and usefulness of the buffer-memory technique, a solution of metal diethyldithiocarbamate (DDC) complexes was prepared. Three DDC complexes, bis(diethyldithiocarbamato)copper(II),tris(diethyldithiocarbamato)chromium(III) and tris(diethyldithiocarbamato)cobalt(III), were dissolved in chloroform in concentrations of 1, 1.5 and 1.5% (w/v), respectively. Fig. 4 shows the IR transmittance chromatogram which was obtained by sequential injection of 0.3 μl of the solution into the column, deposition and IR detection at a fixed wavenumber (1265 cm^{-1}). The retention time was

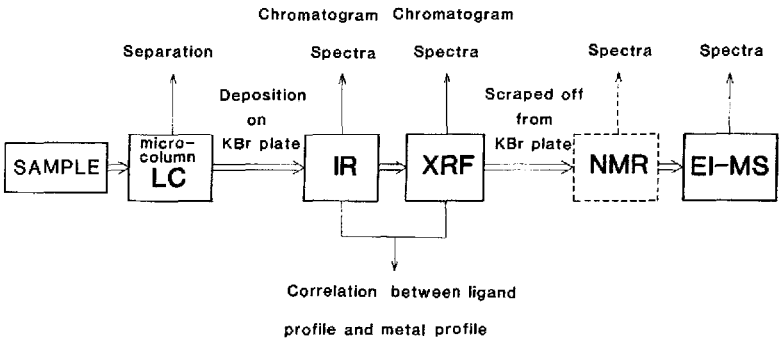
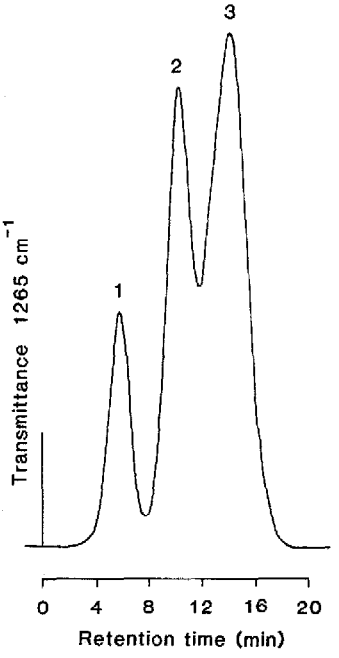


Fig. 3. Analytical scheme for structural elucidation of unknowns using the buffer-memory technique. NMR measurement was not done in this work.

calculated from the KBr plate velocities during the deposition step and the measurement of the IR chromatogram (1.25 mm/min and 20 mm/min, respectively), and the IR chart speed (34.5 mm/min). Spectra of the first, second and third components to be eluted from the column are similar. The spectrum shown in Fig. 5 is of the second peak. The IR spectra of metal N,N-dialkyldithiocarbamates have been reported previously[28] and it is possible to assign some of the bands. For example, the thiouried band near 1500 cm^{-1} is very characteristic of the ligand and indicates considerable double-bond character in the sulphur–nitrogen bond. The detailed spectral assignments are not given here.



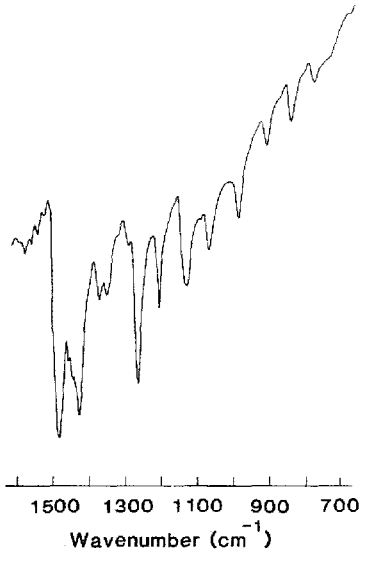


Fig. 4. IR chromatogram from a mixture of three diethyldithiocarbamate complexes. Mobile phase: benzene; flow-rate, 8 μl/min.

Fig. 5. IR spectrum of the second component in Fig. 4. Spectrometer: A-3.

LC–XRF. A previous paper from our laboratory[29] reported the detection limits of transition metals by a proton introduced X-ray excited fluorescence spectrometry (pX,X) technique in which KBr disks were used as backing materials. Although (pX,X) was first reported by Lin *et al.*[30] for the analysis of trace amounts of cobalt present in nickel coins, this is a general method with potential utility for trace element analysis of materials containing large amounts of neighbouring elements. The usefulness of KBr backing materials in the (pX,X) experiment is readily apparent. Since bromine cannot be excited by X-rays from elements with mass numbers lower than that of bromine, such as germanium and gallium, the selection of such excitation sources permits highly sensitive detection of transition metals deposited on KBr. A system employing such backing materials, where the first X-ray is emitted from a tungsten anode X-ray tube, is now available commercially, and was used for the present application.

X-Ray spectra can be measured without removing the LC peak of interest from the KBr plate. The memorized plate is placed in a simple holder made of acrylic resin and moved manually through intervals as small as 1 mm in the Ge *K* X-ray beam to obtain the X-ray fluorescence spectra. The XRF spectrometer employed is ot an energy-dispersive type and enables simultaneous multi-element detection. One of the spectra obtained in this way is shown in Fig. 6. The fluorescence peaks of Cr, Cu, Al and K, together with the germanium scattering peak, are clearly visible. The aluminium peaks originate from the material of beam coursing. (The surroundings of the secondary target are made of aluminium, from which the Al peak originates). For normalization purposes, the peak area of the aluminium fluorescence was chosen. The peak area of each analyte fluorescence was plotted against the retention time.

Fig. 7 shows the resulting metal chromatograms for each analyte metal. Although some peak broadening, which can be mainly attributed to the use of an X-ray beam mask which was larger than the width of the aperture used in the IR experiment, can be seen, the peak maxima coincide in position with those of the IR

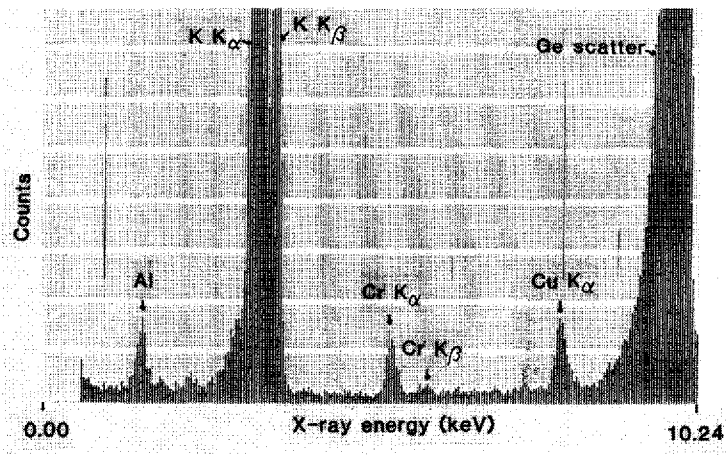


Fig. 6. XRF spectrum obtained through excitation of the species memorized on a KBr plate with Ge *K* X-rays. Counting time (live time): 100 sec. The data obtained from this figure are denoted by arrows in Fig. 7.

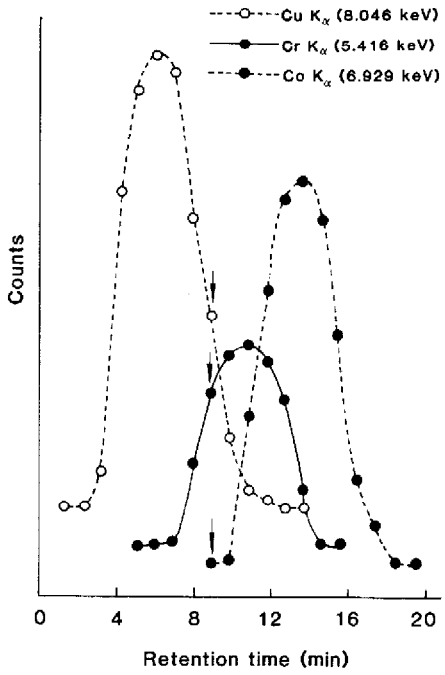


Fig. 7. Metal chromatograms. See text for details.

chromatogram (see Fig. 4). A comparison between the two sets of chromatograms implies that the peaks labeled 1, 2 and 3 in Fig. 4 are due to copper-, chromium- and cobalt-containing species, respectively.

Mass spectrometric identification. Following the XRF measurements, the structure of the deposited components can be confirmed by mass spectrometry. The peaks were scraped off the plate with a clean blade and introduced with a direct insertion probe into the ion source. The mass spectrum of each peak is shown in Fig. 8, together with the spectra of authentic samples. As expected, the spectra are in excellent agreement. Molecular ions appear in the three mass spectra. Fragment ions of diagnostic value are found in all cases at $(M - 148)$, indicating release of one ligand from the molecular ions. A peak at $(M - 7)$ appeared only in the mass spectrum of the third peak, and may result from metal exchange with nickel in the ion source.

The sample constituents used in this work are all coloured, but by referring to the IR chromatogram and/or metal chromatogram colourless constituents could also be scraped off. If a more precise identification to those peaks had been required, nuclear magnetic resonance (NMR) spectra could have been taken prior to the MS analysis (see Fig. 3). Commercially available pulse FT-NMR instruments are sensitive enough to yield usable spectra of the order of a few micrograms of DDC complexes[31].

CONCLUSIONS

We believe that a new dimension has been added to spectrometric detection

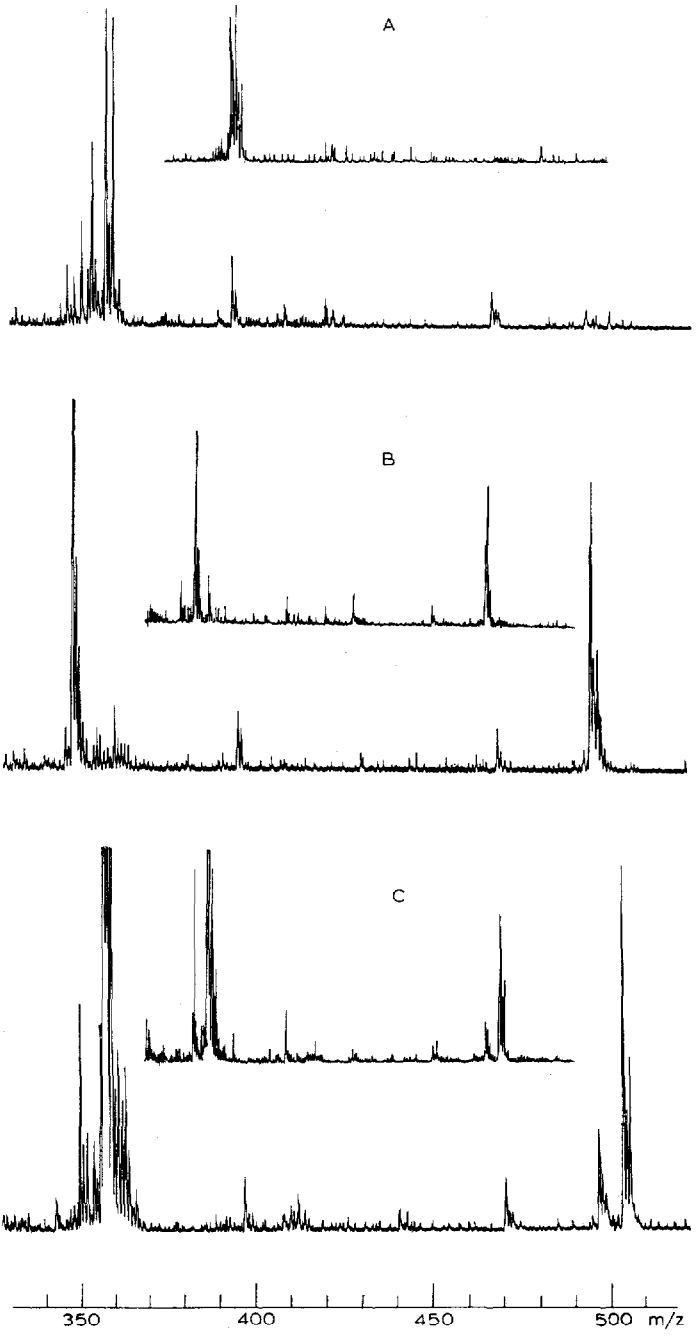


Fig. 8. Mass spectra of the memorized species and (on a smaller scale) of authentic samples. A = First peak; B = second peak; C = third peak, in Figs 4 and/or 7.

and identification of LC separated species. The buffer-memory technique provides some benefits in IR absorption detection as well as in metal detection. To our knowledge, no previous attempts have been made to combine LC with XRF. Inductively coupled plasma atomic emission spectrometers have undoubtedly the most potential among metal specific detectors. Its use, however, has been limited to LC with aqueous solvents as mobile phase, except in three cases[32–34]. When the buffer-memory technique developed originally for the purpose of IR detection is used in conjunction with XRF, it is possible non-destructively to obtain a metal chromatogram which can be related to the IR chromatogram.

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