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Note

Infrared detection of organometallic compounds separated by high-performance liquid chromatography

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Although high-performance liquid chromatography (HPLC) has been used to separate metal carbonyl compounds for a number of years this technique is still not widely used by synthetic chemists. Preparative HPLC has been used to isolate new compounds[1] containing the tricarbonylchromium moiety. Analytical HPLC has been used to monitor the progress of reactions of tricarbonyl(diene)iron compounds[2]. The technique has proved capable of rapidly separating *cis/trans* and *endo/exo* isomers[3]. Both normal-phase[3] and reversed-phase[4] modes of chromatography have been employed. For all these studies detection of column eluates was by absorption in the ultraviolet (UV) region.

Of the many types of detector available to detect column eluates from HPLC separations those based on the absorption of radiation receive the most widespread use and the commonest of these is the UV detector. Providing that a compound possesses a reasonably good chromophore ($\varepsilon > 10^3$ l mol^{-1} cm^{-1}) detection by monitoring a specific wavelength ($\lambda_{max.}$) in the UV region is possible. However, the broadness of absorption bands in the UV effectively precludes the selective or specific detection of compounds of interest. Thus, for example, the isolation of a component of interest from a mixture by selectively detecting it in a preparative LC system is difficult to achieve if detection in the UV is used. The lack of specificity of UV spectra is clearly demonstrated in Table I which lists details of the UV spectra of several ruthenium carbonyl compounds. There is little variation in $\lambda_{max.}$ between these compounds and the broadness of the bands means that all compounds would respond to detection anywhere in the range 210 to 260 nm. (Note: the values of $\lambda_{max.}$ quoted are those associated with the polynuclear ruthenium moiety and not those which may be attributed to the organic fragment.)

In contrast infrared (IR) spectroscopy offers considerable potential as a selective detection technique because of the relatively narrow band width of IR absorption bands. This particularly applies to functional groups which are characterised by strong bands, for example $\gamma_{C\equiv O}$, $\gamma_{C\equiv N}$ and γ_{B-X}. Thus monitoring of column eluates in the IR region at a selected frequency characteristic of a particular compound or functional group allows detection of that compound and discrimination against other components present in the mixture. We now report briefly on our studies using an IR spectrophotometer for the selective detection of organometallic compounds separated by HPLC.

TABLE I

UV SPECTRAL DATA OF POLYNUCLEAR RUTHENIUM CARBONYL COMPOUNDS

Compound No.	*Compound*	$\lambda_{max.}$ *(nm)*	$\varepsilon_{max.}$ *(l mol^{-1} cm^{-1})*
1	$Ru_3(CO)_{12}$	238	14,230
2	$[(CH_3)_3Si]_3C_8H_3Ru_3(CO)_8$	222	19,150
3	1-$[(CH_3)_3Si]C_8H_5Ru_3(CO)_8$	222	17,250
4	2-$[(CH_3)_3Si]C_8H_5Ru_3(CO)_8$	222	19,050
5	$(CH_3)_3SiC_8H_7Ru_2(CO)_5$	234	6,540

Compounds were chromatographed on a silica (10 μm) column (25 cm × 4 mm I.D.) and eluted with hexane at 2 ml min^{-1}. The detection wavelength was 240 nm. A typical separation is shown in Fig. 1. The column contained approximately 2700 effective theoretical plates.

To detect compounds by IR spectroscopy the sample cell of a conventional IR spectrophotometer was modified to reduce its volume to *ca.* 100 μl and to permit the column eluate to flow through the cell whilst it was located in the spectrophotometer. The instrument was operated in the single-beam mode at a series of a pre-selected frequencies. Unfortunately the modified cell permitted only a low energy transmis-

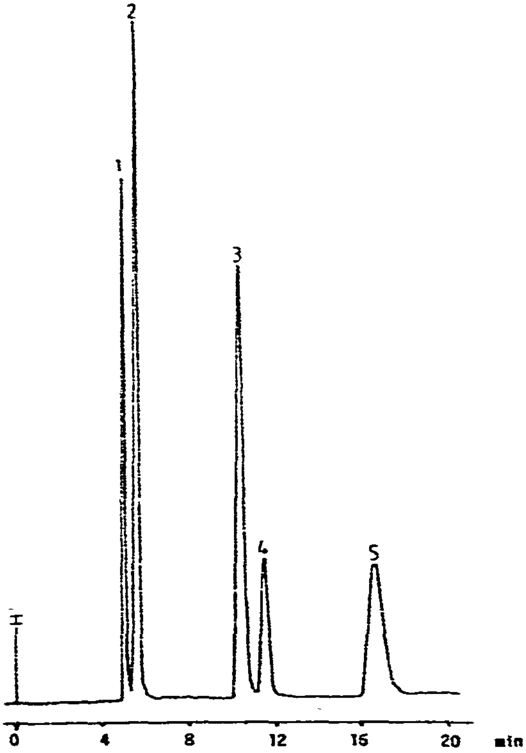

Fig. 1. Separation of ruthenium carbonyl compounds on 10-μm silica. Eluent: hexane, 2 ml min^{-1}. Detector wavelength 240 nm. For peak identification see Table I.

TABLE II

DETECTOR FREQUENCIES FOR IR MONITORING OF COLUMN ELUATES

*Chromatogram code**	*Wavenumber (cm^{-1})*	*Associated compounds*
A	1975	5
B	2010	2, 3, 4, 5
C	2030	1, 2, 3, 4
D	2060	1
E	2080	2, 3, 4

* *F* = 240 nm, UV detection.

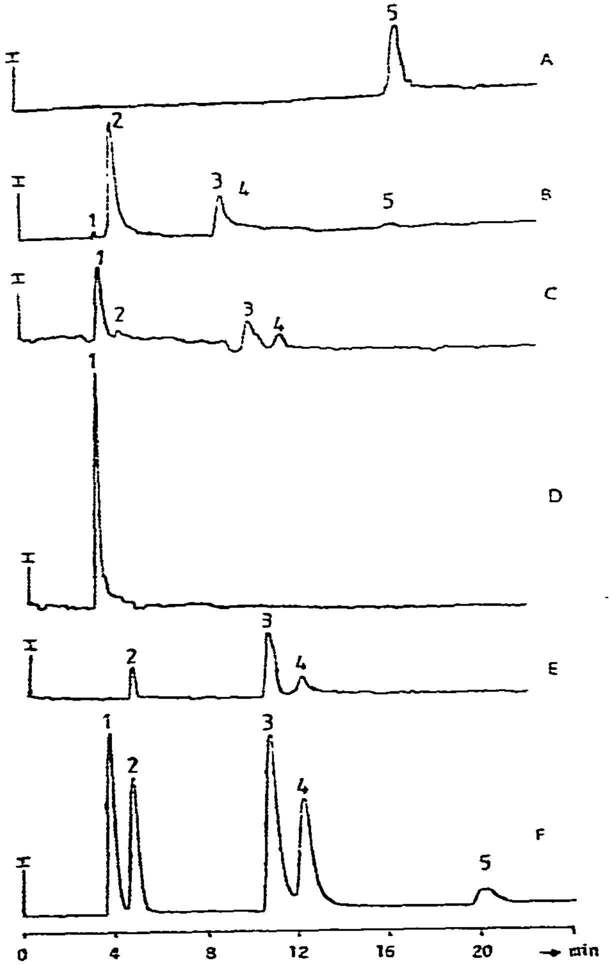

Fig. 2. IR detector response (A–E) for various frequencies and UV detector response (F) to polynuclear ruthenium carbonyl compounds separated by HPLC.

sion and therefore a low signal-to-noise ratio resulted. This modified IR detector was placed in series after the UV detector. Column eluates were thus detected firstly in the UV region and secondly in the IR region. A dual-pen recorder allowed the simultaneous monitoring of both responses.

Table II lists the pre-selected frequencies used together with the compounds which are associated with absorption at the particular wavelength. Fig. 2 summarises the results obtained when a mixture of the five carbonyl compounds was chromatographed and detected at various points in the IR spectrum.

In spite of the poor performance of the IR detector discrimination between the compounds was achieved. For example, monitoring the column eluate at 1975 cm^{-1} (trace A), detects only the compound 5 [$(CH_3)_3SiC_8H_7Ru_2(CO)_5$]. This absorption is associated with the bridging carbonyl group present in this compound. In contrast, monitoring at 2080 detects only trimethylsilyl substituted pentalene compounds (2, 3 and 4) bonded to an $-Ru_3(CO)_8$ fragment. Perhaps the clearest example of selective detection occurs when the column eluate is monitored at 2060 cm^{-1} (trace D). For this case only $Ru_3(CO)_{12}$ (compound 1) is detected. Thus is clear that IR detection in LC although less sensitive than UV detection, can be used to selectively detect discrete components in a complex mixture. For a situation where detector sensitivity is not important IR detection provides a powerful tool for the isolation of specific compounds from complex mixtures by preparative or sem-preparative HPLC. By this technique interference from other, unwanted, compounds present in the mixture can be avoided.

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