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### Determination of carbonyl compounds in an Australian (Rundle) shale oil

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Shale oils are complex mixtures of organic compounds and their fractionation into compound classes has been extensively studied in recent years<sup>1-6</sup>. Although the separated classes have been characterized, some of them have been less thoroughly investigated than others. Shale oil contains relatively large amounts (up to 15%) of carbonyl compounds but the carbonyl fraction has not been adequately characterized. The major component of the oils studied is a homologous series of 2-alkanones<sup>1-6</sup>. In addition, varying amounts of 3-alkanones<sup>2,4,5</sup>, alkenones<sup>4</sup> and phthalate esters<sup>4</sup> have been detected. A methyl cyclopentanone, a trimethyl cyclohexanone and a substituted benzoquinone have been identified<sup>4</sup>, but little else is known about the carbonyl species.

The most common method for isolation of the carbonyl-containing fraction has been liquid chromatography (column or thin-layer) followed by compound identification using gas chromatography (GC) and/or GC-mass spectrometry (MS)<sup>1-6</sup>. However, the chain lengths of the relatively involatile carbonyl compounds observed suggests that many lighter components have been lost during the isolation and work-up. An approach that should avoid these losses is through the use of a derivatization-extraction method.

The Girard reagents, trimethylammonium acetohydrazide chloride (Girard-T) and pyridinium acetohydrazide chloride (Girard-P), have been used extensively for the extraction of carbonyl-containing material from complex organic matrices<sup>7</sup>. They react with aldehydes and ketones to form water-soluble hydrazones, thus providing a facile separation route with hydrophobic materials such as shale oil. In this paper we report the application of the Girard-T reagent to the extraction of carbonyl compounds from a wide-boiling range (100-400°C) shale oil and present the first detailed characterization of the carbonyl compounds found in such an oil.

## EXPERIMENTAL

### *Shale oil*

Oil (boiling range up to 400°C) produced by Lurgi-Ruhrgas retorting from Rundle oil shale (Queensland, Australia) was supplied by Southern Pacific Petroleum, N.L. Analysis: C, 85.4%; H, 11.5%; N, 1.1%; O, 0.9%; S, 0.9%; and ash 0.2%.

### *Carbonyl extraction*

Shale oil (5 g), Girard-T reagent (1 g; Fluka, recryst. from ethanol) and acid catalyst (0.5 g; Amberlite IRC-50 ion-exchange resin) were combined with 100 ml of dichloromethane-methanol (1:1, v/v) and the mixture was refluxed vigorously for 3 h.

The mixture was cooled, filtered, and extracted with water. The aqueous extract was back-extracted with dichloromethane, acidified with conc. hydrochloric acid (to pH 1–2) and stirred overnight. The carbonyl compounds so liberated were extracted into dichloromethane and traces of acid were removed by washing with water. The solvent was then removed under a gentle stream of nitrogen. The Girard-T extract amounted to 8–9% (w/w) of the original oil.

### *GC and GC-MS*

GC of the extract was carried out on a Varian 3700 instrument with a SGE 14 m  $\times$  0.2 mm I.D. SE-30 wall-coated open tubular (WCOT) column and flame-ionization detection. The temperature program was; 40°C (1 min) to 280°C (hold) at 10°C min<sup>-1</sup>.

GC-MS analysis was done on a Hewlett-Packard 5995A apparatus equipped with a SGE 50 m  $\times$  0.2 mm I.D. SE-30 WCOT column. Compound identifications were made by interpretation of the fragmentation patterns and by comparison with the U.S. Environmental Protection Agency-National Institutes of Health library. Mass spectral assignments were confirmed by retention times where standard compounds were available.

## RESULTS AND DISCUSSION

The procedure used varied from the standard Girard extraction. The use of a dual solvent system (dichloromethane-methanol) was adopted to overcome initial difficulties in partitioning the aqueous and organic phases and to allow solubilization of both the oil and the reagent. A cation-exchange resin<sup>8</sup> rather than acetic acid was used to provide the acid catalyst for the derivatization reaction. In our hands, acetic acid gave good yields but results which were not satisfactorily reproducible. In addition, it was difficult to remove and persisted through the various extractions, contaminating the final product. Furthermore, acetate formed in the neutralization step buffered the acid added in the hydrolysis step, increasing the volume of liquid to be handled.

Use of a cation-exchange resin resulted in a simpler and more reproducible system. When reaction was complete, the resin was removed by filtration, avoiding the problems associated with acetic acid.

The carbonyl extract average 8–9% (w/w) of the original oil. The compounds identified are listed in Table I and a gas chromatogram of a typical extraction is shown in Fig. 1. The unlabelled series in Fig. 1 comprised paraffinic contaminants.

The major components were of a homologous series of 2-alkanones. 2-Alkanones have been identified as the main carbonyl-containing constituents in a number of shale oils<sup>1–6</sup>. The advantage of the derivatization-extraction procedure was demonstrated in the isolation of members of the series down to 2-butanone. This was the expected limit of extraction due to the solubility of 2-propanone (acetone) in water.

TABLE I  
PEAK ASSIGNMENTS FOR CARBONYL EXTRACT

ms = Mass spectral identification; rt = assignment confirmed by retention time of pure standard.

Peak No.	Compound	Identification	Peak No.	Compound	Identification
●	<i>n</i> -Alkyl methyl ketones ( <i>n</i> = 2-27)	ms <i>n</i> = 2-11, rt	13	1-Cyclohexenyl methyl ketone	ms
▼	2- <i>n</i> -Alkyl cyclopentanones ( <i>n</i> = 1-10, 14)	ms	14	C <sub>3</sub> -Cyclohexenone	ms
1	3-Methyl-2-butanone	ms, rt	15	2-Methyl acetophenone	ms, rt
2	Cyclopentanone	ms, rt	16	Propiophenone	ms, rt
3	3-Hexanone	ms, rt	17	3-Methyl acetophenone	ms, rt
4	Cyclohexanone	ms, rt	18	4-Methyl acetophenone	ms, rt
5	3-Heptanone	ms, rt	19	C <sub>2</sub> -Acetophenone	ms
6	2-Methyl-2-cyclopentanone	ms	20	Butyrophenone	ms, rt
7	4-Ethyl cyclohexanone	ms	21	Methyl indenone	ms
8	3-Methyl-2-cyclopentanone	ms	22	1-Indanone	ms, rt
9	3-Methyl-2-cyclohexenone	ms	23	Methyl-1-indanone	ms
10	Cycloheptanone	ms, rt	24	4,5,6,7-Tetrahydro-1-indanone	ms
11	C <sub>2</sub> -Cyclopentanone	ms	25	1-Tetralone	ms, rt
12	Acetophenone	ms, rt	26	Pentyl phenyl ketone	ms
			27	C <sub>3</sub> -Tetralone	ms
			28	Hexyl phenyl ketone	ms
			29	Heptyl phenyl ketone	ms

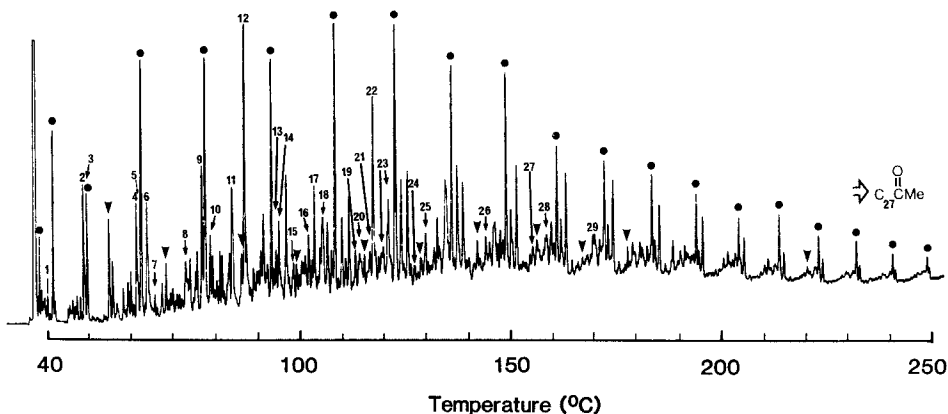


Fig. 1. Gas chromatogram of a Girard-T extract of shale oil. Conditions were: 14 m  $\times$  0.2 mm I.D. SE-30 vitreous silica WCOT column, temperature programmed from 40°C (1 min) to 280°C (hold) at 10°C min<sup>-1</sup>. Me = Methyl.

The series extended to C<sub>29</sub> as indicated by earlier liquid chromatographic studies<sup>3,6</sup>.

Two 3-alkanones (3-hexanone and 3-heptanone) were present in small quantities and were positively identified (although not resolved in the chromatogram in Fig. 1 they were separated on a 50-m column). 3-Alkanones have been observed in other shale oils, usually in small quantities, although an extensive series (C<sub>7</sub>–C<sub>29</sub>) has been identified in a Green River shale oil<sup>4</sup>.

A large number of carbonyl compounds not observed previously in shale oil were extracted by the Girard-T method. A series of alkyl phenyl ketones was present. Acetophenone, propiophenone and butyrophenone were identified and tentative identifications were made of higher homologues; pentyl-, hexyl- and heptylphenyl ketones. The *ortho*, *meta* and *para* isomers of methyl acetophenone were also identified. Significant quantities of 1-indanone, 4,5,6,7-tetrahydro-1-indanone, and 1-tetralone were found. It is of interest that of the parent hydrocarbons, indane was present in the original oil while tetralin was not<sup>6</sup>.

Cyclic ketones were prominent in the lighter fractions of the carbonyl extract. Cyclopentanone, cyclohexanone and cycloheptanone were all present in reasonable quantities; none of these have been identified before in any oil; shale or crude. Cycloheptanone is the first seven-membered ring compound identified in shale oil. Seven-membered rings are most uncommon in crude oils and have been detected only in minute amounts<sup>9</sup>. A series of substituted cyclopentanones was also detected. These have a single *n*-alkyl substituent and examination of the mass spectra of the first two members of the series indicated that they were 2-*n*-alkylcyclopentanones. The alkyl substituent varied from one to at least fourteen carbon atoms in length.

The use of a derivatization agent facilitates the extraction of carbonyl compounds which have not previously been identified in shale oil. The extraction procedure is particularly effective in the isolation of volatile compounds which are not observed when liquid chromatography (high-performance, column, thin-layer) is used for fractionation. Therefore, although liquid chromatography remains the most powerful technique for chemical class fractionation of complex oils, selective extrac-

tion methods such as that using the Girard-T reagent still offer advantages in specific cases.

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