

INVESTIGATION OF THE COMPOUNDS CAUSING THE OFFENSIVE SMELL OF PARAFFIN WAX

By

P. SIKLÓS and L. NAGY

Department of Chemical Technology, Technical University, Budapest

(Received July 5, 1976)

Presented by Assoc. Prof. Dr. I. SZEBÉNYI

The paraffin wax slabs produced in petroleum refineries often have an offensive smell caused presumably by oxygen-containing compounds [1]. The compounds involved can be aldehydes, ketones, carbonic acid or esters. In all these compounds oxygen is present in the form of the carbonyl group $C = O$.

The detection of substances causing the smell of paraffin wax has been the subject of much research work. FRIEDRICH and co-workers [1] also assumed the carbonyl group to be primarily responsible, and attempted to correlate its amount to the strength of the smell. They used paraffin wax from Romashkino crude in their studies. The odour compounds having a polar nature, were adsorbed on a Zeosorb 13X molecular sieve, and the desorbed product rich in odorous substances was studied by means of IR spectrophotometry. From the IR absorption of the carbonyl group they concluded on the amount of odorous substances.

Experimental

Analytical determination of the carbonyl group

The study of paraffin wax samples obtained from Romashkino (Soviet Union) and Algyő (Hungary) crudes started with carbonyl group determination. The analytical method consisted essentially in concentrating and subsequent IR measurement of the compounds containing carbonyl groups. These compounds (and, in addition, other polar compounds) were concentrated by adsorption of Molfilit KX-130 and Linde 13X molecular sieves.

Forty to 80 g of the paraffin wax sample were weighed into a glass-stoppered spherical flask and 20 to 25% by weight of the molecular sieve were added. The flask was then placed in an electrically heated sand bath and held at 80 to 100 °C for 3 hours, frequently shaking the flask. After this treatment the molten paraffin wax was poured off. Residual paraffin on the surface of the adsorbent was removed by washing three times with n-heptane. Sub-

sequently the molecular sieve was placed into a Soxhlet apparatus and extracted with acetone for 6 hours. The amount of acetone used in this operation was about 250 cm³. Its role was to desorb and retain in solution the substances adsorbed on the molecular sieve. After desorption was completed, acetone was distilled off in vacuum and the residue was placed for two hours under a 250 W infrared lamp to remove traces of acetone. This operation finally yielded a yellowish solid with a strong unpleasant smell.

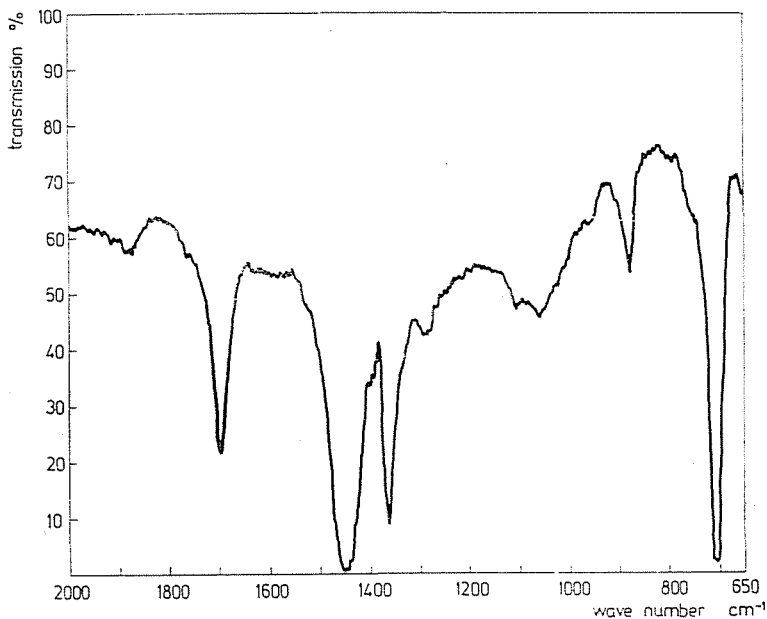


Fig. 1. Infrared spectrum of the substance desorbed from the molecular sieve

To check the reliability of this analytical method, the paraffin poured off after the adsorption operation and considered inodorous, has been repeatedly treated with the molecular sieve as described above. After extraction with acetone and removal of the solvent, a solid residue was again obtained, but this substance was colourless and relatively inodorous. IR spectra of the residue after the first treatment and after the repeated treatment are presented in Figs 1 and 2, respectively.

In Fig. 1, extinction at 1710 cm⁻¹ characterizing the carbonyl group is clearly observable, while no extinction at this wave number occurs in Fig. 2. This finding demonstrates that a single treatment with the molecular sieve is satisfactory for separating carbonyl-containing substances.

The figures also allow to state that after the desorption with acetone, the solvent removal is complete, since otherwise the carbonyl band should be present in Fig. 2.

For quantitative determinations solutions were from paraffin oil and varying amounts of stearic acid. The well-defined CO content of the latter proved suitable for quantitative determinations.

Experiments had also to be carried out to find a suitable IR spectrometry technique, since the test material was, on the one hand, solid paraffin wax, and on the other hand, a solution in paraffin oil. The technique finally applied was to introduce the molten wax and the liquid oil, in appropriate

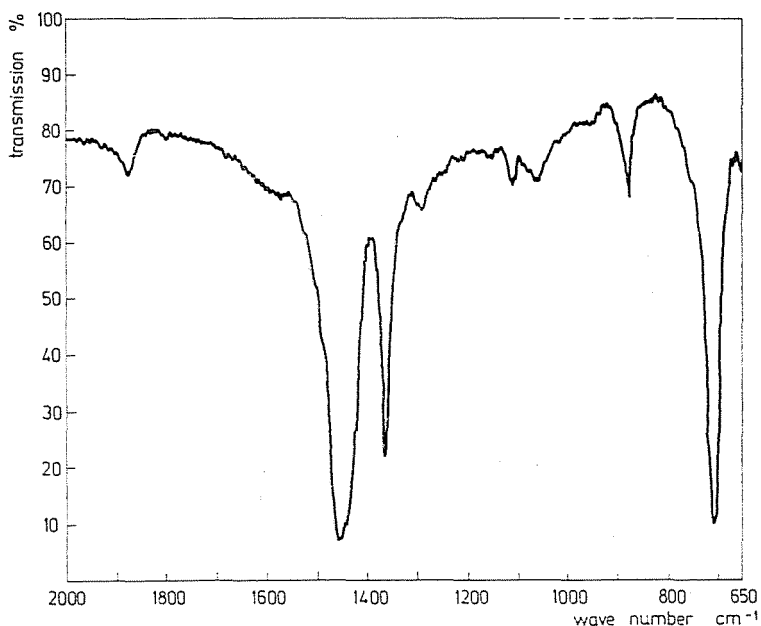


Fig. 2. Infrared spectrum of odorless paraffin wax

layer thicknesses, into potassium bromide cuvettes. A Unicam SP 200 spectrophotometer was used for measuring extinction at the 1710 cm^{-1} absorption band of the carbonyl group using the base line method.

By means of the standard solutions containing known amounts of stearic acid, the following relationship was found for the quantitative determination of the carbonyl group:

$$>\text{C}=\text{O} \text{ (p. p. m.)} = 0.46\epsilon \frac{0.133}{h} s \cdot 10^2$$

where

$>\text{C}=\text{O}$ is the carbonyl content of the paraffin wax sample in p.p.m.,
 ϵ is the extinction of the desorbed extract rich in odorous compounds,
 s is its percentage by weight in the paraffin sample used for adsorption,
 h the thickness of the cuvette used for IR measurement, mm,

Table 1
Carbonyl group content of various paraffin wax samples

No. of sample	Desorbed substance % by wt	Extinction at 1710 cm^{-1}	C=O content of sample, p.p.m.
1	3.7	0.231	39
2	3.2	0.328	49
3	4.0	0.150	28
4	3.4	0.269	42
5	4.4	0.339	69
6	3.8	0.210	36
7	3.4	0.486	76
8	2.2	0.311	31
9	4.4	0.123	25
10	5.4	0.109	28
11	4.0	0.122	23
12	3.0	0.108	16

0.133 thickness of the cuvette used for calibration measurement, mm, and 0.46 the factor found by calibration from the relationship between carbonyl content and extinction.

The carbonyl contents of the paraffin samples have been compiled in Table 1.

Study of the structure of the substances causing smell

In the followings, it was attempted to clarify the structure of the substances causing the bad smell. The extracts used for the determination of carbonyl content have been repeatedly treated with molecular sieves as described in the foregoing.

The final concentrate after several adsorptions had a very offensive smell exhibited a carbonyl content as high as 6000 p.p.m. investigated by IR spectrometry and NMR method.

For infrared spectrometry, a SPEKTROMOM 2000 instrument was used. The IR spectrum is shown in Fig. 3.

In addition to characteristic absorption bands of paraffinic hydrocarbons and to a strong carbonyl band at 1710 cm^{-1} , extinction at 3300 to 3500 cm^{-1} indicates the presence of OH groups, which, together with the aliphatic carbonic acid and appearing at 1260 cm^{-1} , demonstrates that the sample contains carbonic acids. From the band at 1600 cm^{-1} characteristic for aromatic structures, one may conclude on the presence of a small amount of aromatic compounds.

For NMR measurements a PERKIN-ELMER R 12 high-resolution instrument was applied, using tetramethylsilane (TMS) as internal standard at 60 MHz. The sample was dissolved in carbon tetrachloride.

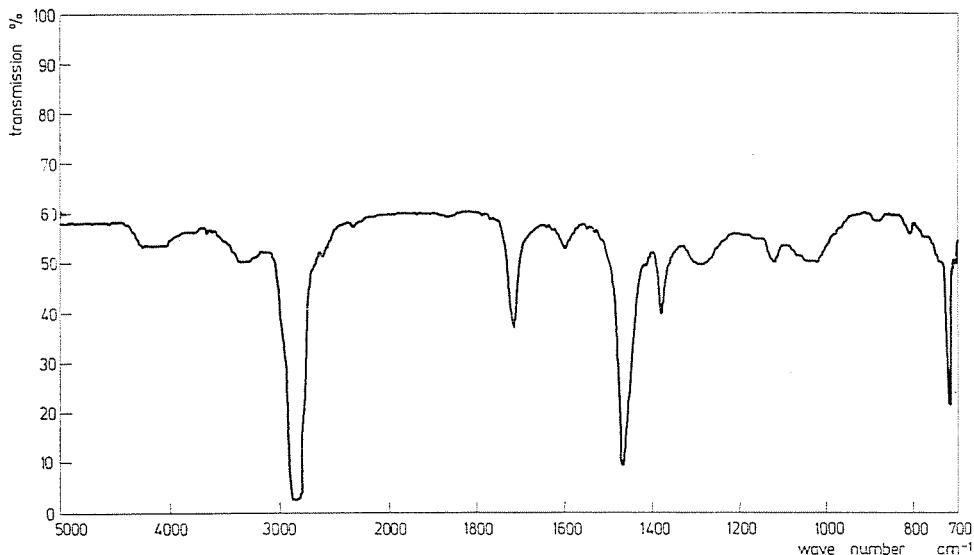


Fig. 3. IR spectrum of the substance repeatedly treated with molecular sieve

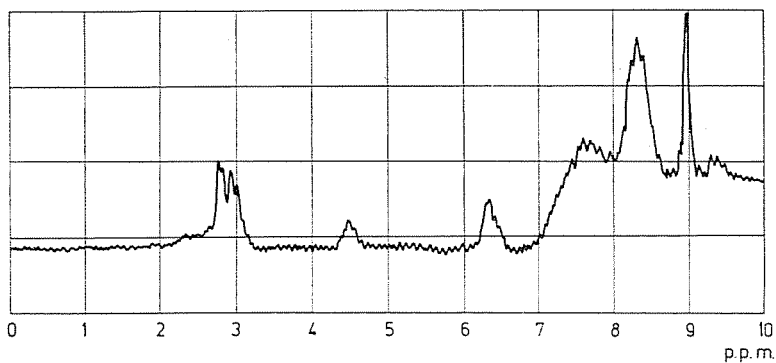


Fig. 4. NMR spectrum of the substance repeatedly treated with molecular sieve

The NMR spectrum of the extract obtained after repeated treatment with molecular sieve is presented in Fig. 4.

The signal group at $\tau = 9.1$ p.p.m. can be assigned to the terminal $-\text{CH}_3$ groups of the paraffins, while the signals corresponding to the $-\text{CH}_2-$ and $-\text{CH}-$ groups forming the paraffin chains appear in the $\tau = 8.5$

9 p.p.m. range. The signals around $\tau = 2.8$ p.p.m. suggest the presence of small amounts of aromatic (or possibly quinonoid) protons. Proton resonance of olefinic hydrocarbons appears at $\tau = 4.5$ p.p.m.

The signal around $\tau = 6.3$ p.p.m. is presumably assignable to protons located near electrophil substituents (oxygen, sulphur). Several protracted signal groups in the $\tau = 7.1$ to 8.4 range demonstrate above all the presence of aliphatic carbonyl groups.

Acknowledgements

The authors wish to express their gratitude to the Danubian Petroleum Refinery Enterprise for financial aid to the research work, and to Mr. Gyula Nagypataki, head of department, for his valuable suggestions.

Summary

The amount of carbonyl-containing substances present in solid paraffin waxes has been determined. The first step in the analytical procedure was to concentrate the compounds causing the smell by means of molecular sieve. The infrared spectrum of the concentrate was then used for quantitative determination of the carbonyl group by means of calibration measurements.

Other polar compounds present in the sample were investigated after repeated adsorption treatment on molecular sieves.

Based on IR and NMR spectra, it could be stated that the substance separated from paraffin wax slabs and carrying the offensive smell includes — in addition to oxygen-containing compounds — aromatic and olefinic hydrocarbons.

Reference

1. FRIEDRICH, W.—KAHLERT, E.—BERG, K.: Erdöl und Kohle, **24**, 78 (1971).

Dr. Pál SIKLÓS }
Dr. Lajos NAGY } H-1521 Budapest