This is probably caused by the association of the molecules with functional group having a strong ability to hydrogen bond. Formation of larger associates decreases the possibility of hydrogen bonding interactions with test solutes. Similar results were reported earlier by Boduszynski [4]. However, the positive values found for n-alkanes suggest the presence of “polar” component, reducing the ability to non-specific/dispersive interactions.

A similar situation is observed for the slack wax fractions separated from all the oil residues. For these fractions, positive \( \kappa_{12}^e \) values may be attributed to the dominating presence of higher hydrocarbons [17], i.e. species which do not possess functional group and whose intermolecular interactions with test solutes are reduced to non-specific-dispersive interactions. The positive values found for n-alkanes on the slack waxes may be caused by the reduced possibility for dispersive interactions.

The influence of the number of carbon atoms in the n-alkane probes upon the \( \kappa_{12}^e \) values is presented in Figure 2. Highest positive values of \( \kappa_{12}^e \) are observed most often for fractions separated from the Flotta-Blend oil. For the B-6 oil, only heptane and slack wax fractions gave high values. The lowest \( \kappa_{12}^e \) values were found most often for fractions separated from the Pipe Oil.

The Flory-Huggins interaction parameter is a measure of mutual solubility of two species: solvent (stationary phase consisting of an oil fraction) and solute (test probe). It is well known that the difference between the solubility parameter of a solute/solvent pair is a criterion for the selection of the proper solvent for a given polymer. Relationships existing between \( \kappa_{12}^e \) and \( (\delta_2 - \delta_1) \) value are presented in Figure 3. The best mutual solubility was found when \( (\delta_2 - \delta_1) \) value was positive and in the range 0–3.5 \( (1 \text{ mol}^{-1})^{1/2} \) which agrees well with literature data (i.e. the difference should be in the range 0–0.5 \( (\text{cal} \text{ mol}^{-1})^{1/2} \)).

Conclusions

The Flory-Huggins interaction parameter \( \kappa_{12}^e \) has been determined for fractions separated from vacuum distillation residues of three different crude oils. The strongest interactions with the separated fractions when used as liquid stationary columns in inverse gas chromatographic experiments were found for C1-C9 aliphatic hydrocarbons, pyridine, 1,4-dioxane and benzene. Practically, no interactions were found for alcohols, ketones and nitro compounds. Fractions separated from two vacuum distillation residues (B-6 and Pipe Oil) exhibit similar properties when expressed by \( \kappa_{12}^e \), i.e. interactions of approximately similar order with the same test solutes. This may indicate that these fractions were separated from crude oils of similar chemical character.

Fractions separated from Flotta-Blend oil exhibit significantly different properties.

On the basis of the results obtained for a large group of test solutes the \( \kappa_{12}^e \) parameter may be used for a discussion of the chemical nature of the crude oils from which the fractions were separated.

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References

Fast Headspace Analysis with Short Microcapillary Columns

M. V. Russo
Dipartimento di Chimica, Università “La Sapienza” Roma, P.le Aldo Moro 5, 00185 Roma, Italy

Key Words
Gas chromatography
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Summary
A new method of analysis using headspace gas chromatography with microcapillary columns is proposed. Small diameter (50 μm I.D.) fused-silica capillary columns with non-extractable SE-54 and PS-255 poly-siloxane stationary phases were used for the analysis of low boiling organic compounds. The small diameter columns possess the usual very high efficiency so that the method can be employed for the headspace analysis of complex mixtures. The use of short microcolumns reduces the analysis times in comparison to conventional capillary columns. Good performances were obtained in the analysis of volatile compounds in some lemon essential oil, perfumes, and water samples.

Experimental
Reagents
N-pentane, n-hexane, n-heptane, benzene, toluene, methylcyclohexane, p-xylene, m-xylene, o-xylene, isopropylbenzene(cumene), n-octanol, methyl alcohol, dichloromethane, trichloromethane, 1,1,1-trichloroethane, tetrachloromethane, trichloroethene and tetra-chloroethene were all from Carlo Erba (Milan, Italy). Sabine, α-thujene, α-pyrene, camphene, β-pyrene, myrcene, β-cymene, limonene, γ-terpinene, terpinolene, linalool, citronellal, nerol, 4-terpinolene, α-terpineol, neral, linalylacetate, geranylacetate, bornylacetate, citronellylacetate, geranial, nerylacetate, β-cariofilyl- lene, bergamotene and humulene were all from Carl Roth (Germany). The reagents were of analytical-reagent grade with purity ≥ 99 %.
The lemon essential oils of Petit-Grain were supplied by the Experimental Station of Essential Oils of Reggio Calabria (Italy). The perfume samples analyzed were commercial products. Distilled water was prepared in our laboratory.

Introduction
The headspace analysis of volatile organic compounds has received considerable attention in past years and it is seen to compete with the more conventional techniques, i.e. distillation, liquid-liquid extraction and purge and trap, previously used.
In these applications gas chromatographic headspace analysis with packed and capillary columns [1-14] has been used. Because of their high efficiency the utilization of capillary columns has led to the resolution of some very difficult problems in the separation of complex mixtures of volatile compounds.
Usually, static or dynamic headspace analysis is performed with long capillary columns which, as they generally have thick films of stationary phase, results in long analysis times.