

Petroleum inclusions in sedimentary basins: systematics, analytical methods and applications

Ingrid Anne Munz*

Institute for Energy Technology, P.O. Box 40, N-2027 Kjeller, Norway

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Abstract

Fluid dynamics in sedimentary basins is of tremendous interest, both from a scientific and an economic point of view. Integration between fluid inclusion and present-day fluid data provides the time aspect necessary for reconstruction of fluid flow paths, and can be used for mapping fluid dynamics both on a regional basin scale or on the more local scale of petroleum reservoirs. This paper presents a review of analytical and modelling methods for petroleum in fluid inclusions. Essentially, four types of data for petroleum inclusions can be established through analysis and modelling: (1) textures (which give indirect information of the time aspect), (2) fluid composition, (3) fluid properties and (4) pressure–temperature of trapping. During the last decade, development of analytical methods for determination of inclusion fluid compositions has taken place. Traditional correlation studies for characterisation of maturity and source facies may now therefore include fluid inclusion data. The development has also been directed towards an improved understanding of the physical properties of petroleum inclusions. Although these methods are in their early stages concerning precision and accuracy, data necessary for fluid flow modelling, such as fluid densities, viscosities, pressure and temperature, can be estimated. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

In contrast to most magmatic and metamorphic systems, fluid inclusions in sedimentary basins represent one of several available fluid sample types. Trapping of fluid inclusions may occur at different stages of basin development, but is most common in the deeper parts. Integration between fluid inclusion and present-day fluid data, for example, from drill stem test (DST) samples, provides the time aspect necessary for reconstructing fluid flow paths, and

can be used for mapping fluid dynamics on a regional basin scale or on the more local scale of petroleum reservoirs. Aqueous fluids are dominating in sedimentary systems, and are actively participating in diagenetic processes (Goldstein, 2001). The focus of this paper is the less abundant, but economically more important petroleum fluids. Essentially, four main types of data for petroleum inclusions can be established through fluid inclusion analysis and modelling.

- *Textures:* The textures give important information on the time aspect. The methodology is the same as for fluid inclusion studies in other geological environments (Van den Kerkhof and Hein, 2001),

* Tel.: +47-63-80-60-00; fax: +47-63-81-55-53.
E-mail address: ingridm@ife.no (I.A. Munz).

and the objective is to establish the time relationship between (1) diagenetic growth of minerals and trapping of inclusions and (2) different populations of inclusions.

- *Composition:* The composition of petroleum fluids is complex, and emphasis will be given to the characterisation of composition. Compositional information is fundamental both in geological interpretation of fluid source and maturity and in modelling of the fluid phase behaviour in the next two points.

- *Pressure–volume–temperature (PVT) properties:* This relates to the physical properties of the fluid and can be used for modelling the fluid phase behaviour at any pressure and temperature conditions.

- *Pressure and temperature of trapping:* Isochores for petroleum inclusions can be calculated when the PVT properties are known. Additional data from coeval aqueous inclusions are necessary for simultaneous determination of the pressure and temperature conditions of trapping.

This paper describes the analytical methods, which can be used to establish these four main types of data. Analytical methods comprise non-destructive

techniques for characterisation of various properties of single inclusions and destructive, bulk techniques for characterisation of composition. The paper will give an overview of these techniques, but will not discuss specific details in equipment or instrumentation. Applications of the analytical data to fluid correlation studies and PVT modelling will be shown.

2. The nature of petroleum fluids

Petroleum fluids are characterised by their extreme complexity. A classification scheme can be based on chemical or physical properties and depends commonly on the application, whether it is in geology/geochemistry or reservoir engineering. Genetic characterisation of source and maturation of petroleum fluids has been the focus of the research in organic geochemistry for decades, and will not be discussed here. The objective of this section is to provide the necessary background on the relationship between the chemical and physical nature of petroleum fluids for interpretation of fluid inclusion analysis data.

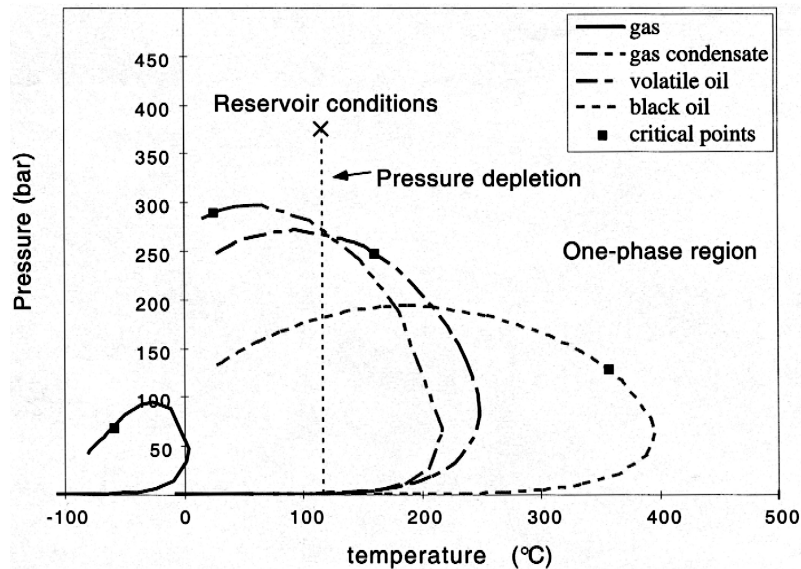


Fig. 1. Classification of petroleum reservoirs. The two-phase envelopes show the region where two petroleum phases may coexist for various types of fluid compositions. Classification of the reservoirs is based on the fluid composition and the original pressure–temperature conditions. In a gas reservoir pressure depletion will never lead to intersection with the two-phase envelope. In a condensate reservoir, pressure depletion will lead to intersection with a dew point curve, and in volatile and black oil reservoirs, to intersection with the bubble point curve.

The main components of petroleum are hydrocarbons, nitrogen–sulphur–oxygen bearing (NSO) compounds and inorganic gases, such as N_2 , CO_2 and H_2S . The hydrocarbons in petroleum can be subdivided according to their structure into: (1) paraffins, which consist of normal and branched alkanes. Alkanes are often called saturated hydrocarbons, since all atoms are connected with single bonds; (2) naphthenes or cycloalkanes, which consist of compounds with cyclic structures. The naphthenes are also saturated compounds, which only contain single bonds; (3) aromatics are compounds which contain cyclic structures with double bonds. The simplest aromatic compound is benzene, C_6H_6 , consisting of a ring structure with six carbon atoms.

The simplest hydrocarbon compound is methane, CH_4 . Methane has a critical point at low temperature and will only exist as a supercritical fluid or gas at geological conditions. As the number of carbon atoms in the molecule increases, the possible ways of combining the atoms increase. Compounds which have the same formula but different structures are called isomers. The number of isomers increases rapidly with increasing number of carbon atoms. Increase in the number of carbon atoms in the molecule also leads to increase in the critical temperature and decrease in the critical pressure. At room temperature, pentane, for example, will exist as a liquid, and compounds with a high number of carbon atoms (e.g. naphthalene, $C_{10}H_8$) will be in the solid phase. The complexity in chemistry of petroleum fluids thus results in an equally complex phase behaviour.

Petroleum accumulations are commonly classified as gas, condensate, volatile oil or black oil reservoirs (Fig. 1). In a gas reservoir, pressure depletion will never lead to intersection with the two-phase envelope. Pressure depletion in a condensate reservoir will eventually lead to intersection with the dew point curve, and in a volatile or black oil reservoir, to intersection with the bubble point curve. Definitions of dew point and bubble point curves have been given by Van den Kerkhof and Hein (2001).

3. Trapping of petroleum inclusions

The principles for secondary migration and filling of reservoirs have been described in a series of

papers by England (1989), England and Mackenzie (1989) and England et al. (1987, 1995). The most important mechanism for migration is bulk transport driven by gradients in petroleum fluid potential. The migration takes place in a series of stringers with dendritic pattern. During filling of the reservoir, the petroleum pore saturation increases, and the reservoir fluids may start to redistribute by processes, such as diffusion and density-driven convection. The models of England et al. show that the time-scale of these processes is substantial, and lateral variations in fluid compositions reflecting the process of filling can be preserved to the present-day.

Trapping of petroleum inclusions can occur along migration pathways or in reservoirs. Due to concentrated exploration activity, most of the documented occurrences of petroleum inclusions have, however, been described from reservoirs. Trapping of petroleum inclusions in reservoirs may occur from the onset of filling to the present-day (or to the time of drainage in case of wells, which are only aqueous at present). Due to the general inhibiting effect of petroleum on cementation, it is, however, likely that trapping mechanisms are most active during filling of the reservoir than at an arbitrary later time, when most of the water has been displaced (Munz et al., 1999a). The inclusions give important constraints on petroleum migration and reservoir filling, and can be used as calibration points for modelling of these processes.

In clastic reservoirs, there is a correlation between petroleum inclusion abundances and porosity and permeability (Oxtoby et al., 1995; Munz et al., 1999a). Most of the petroleum inclusions occur as secondary inclusions within detrital grains (e.g. quartz and feldspars). Oxtoby et al. (1995) find that the distribution and abundance of petroleum inclusions reflect the manner in which the petroleum invades rocks of different permeability, including migration routes below the present oil leg. According to Oxtoby et al. (1995), the correlation between petroleum inclusion abundances and porosity/permeability results from a higher density of migrating petroleum stringers in rocks of good reservoir quality during filling of the reservoir. The inclusion data are thus in agreement with the models of England et al.

Studies of the distribution and abundance of petroleum inclusions in chalk and limestone reser-

voirs have, to the author's knowledge, not been published. Petroleum inclusions in these reservoirs may occur within cemented fractures, recrystallised macrofossils or other types of coarse grained cement (Burruss et al., 1983; Jensenius and Burruss, 1990). The distribution of petroleum inclusions is therefore more irregular than in clastic reservoirs. The local abundance of petroleum inclusions in fracture cement samples can be 2–3 times higher than in sandstones (Munz et al., 1999b).

The timing of reservoir filling/migration relative to the diagenetic sequence can be established by examination of the textural relationship between the host mineral and the petroleum inclusions. Case studies from the North Sea have shown examples of both early (Nedkvitne et al., 1993; Oxtoby et al., 1995; Munz et al., 1998) and recent reservoir filling histories (Munz et al., 1999a). Examples of a contemporaneous relationship between quartz cementation and trapping of petroleum inclusions can be shown from primary petroleum inclusions within the dust rim of quartz overgrowths (e.g. Nedkvitne et al., 1993; Oxtoby et al., 1995). Primary and pseudosecondary petroleum inclusions in fracture cements may give evidence for the presence of petroleum during fracturing and subsequent cementation (Munz et al., 1998). Petroleum migration can be inferred from compositional differences between inclusions in successive growth zones of fracture cement samples (Bodnar, 1990), or from the presence of different populations of inclusions in different generations of cements (Burruss et al., 1983). An example of recent reservoir filling, which was post-dating most of the quartz cementation in a clastic reservoir, was documented from subparallel trails of petroleum inclusions (Munz et al., 1999a). These subparallel trails were continuous throughout the samples, and were cutting across both the detrital and the authigenic part of the quartz grains.

4. Non-destructive analytical methods

4.1. Petrography – identification of petroleum inclusions

A petrographic recognition of petroleum inclusions is typically based on fluorescence behaviour,

colour and the number of phases at room temperature and their relative proportions.

Petroleum inclusions can easily be mistaken with aqueous inclusions. The most rapid and effective way of distinguishing the two fluids is by fluorescence microscopy. When exposed to ultraviolet (UV) light, petroleum emits light in the visible range, whereas aqueous fluids are non-fluorescent. The fluorescence colour of petroleum inclusions reflects compositional information, and the methodology of fluorescence spectroscopy is discussed in more detail below. During an initial petrographic screening, the fluorescence colour easily reveals if the sample material contains one or multiple generations of petroleum inclusions.

Petroleum inclusions are often colourless, but may, in some cases, have a brown colour. The colour is a function of composition and size of the inclusion (Burruss, 1981). Due to the small size of petroleum inclusions, in sandstones typically 5–25 μm , the colour, even in coloured oil can, however, be difficult to observe.

Except for dry gas compositions, petroleum inclusions consist most commonly of two phases, liquid (L) and vapour (V), at room temperature. The proportion of liquid and vapour at room temperature is highly variable, as a function of both composition and density. Inclusions of gas condensate compositions will have large vapour bubbles at room temperature and can fill most of the inclusion, whereas the vapour bubble in volatile or black oil compositions will be smaller and the liquid phase will be dominating. In addition, petroleum inclusions can contain a black solid. An aqueous phase is only visible in inclusions with heterogeneous trapping. An example of the four phases is shown in Fig. 2.

Fig. 3 illustrates how the three properties (i.e. colour, fluorescence colour and the proportion between liquid and vapour at room temperature) can be used as quick, qualitative indicators of composition and density. The inclusion in Fig. 3A shows a relatively small vapour bubble, no colour and a pale bluish fluorescence. This gives an indication of a relatively mature, volatile oil composition. The small size of the vapour bubble leads to an expectation of liquid homogenisation, which can be confirmed by microthermometry. The characteristics of the inclusion in Fig. 3B are very different, with a large

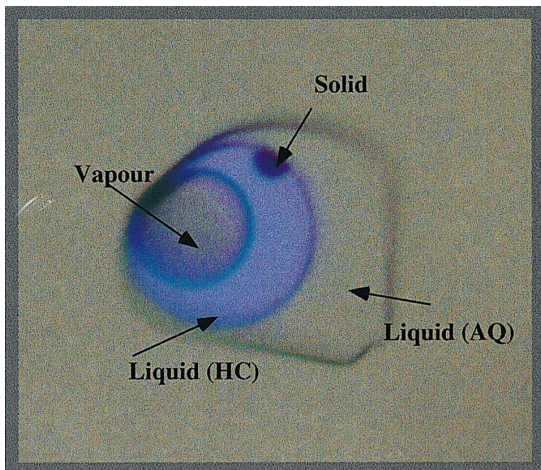


Fig. 2. An example of an inclusion with four phases (HC = petroleum, AQ = aqueous).

vapour bubble and a deep blue fluorescence colour. In this case, vapour homogenisation would be expected, which can also be confirmed by microthermometry. The fluid in this inclusion would classify as a condensate. The third example (Fig. 3C) shows a less mature, oil composition. The relatively immature nature of this inclusion is indicated by the more yellowish fluorescence colour.

4.2. Petrography – relationship to the host mineral

The textural relationship between the petroleum inclusions and the host mineral is essential, when the relative timing between petroleum migration and/or reservoir filling and the diagenetic evolution is to be established. Some ‘classical’ textural occurrences of petroleum inclusions in sedimentary rocks are shown in Figs. 4–6.

The most common occurrence of petroleum inclusions in clastic reservoirs is in secondary trails within detrital quartz (Fig. 4A). As a textural time indicator, these inclusions are often useless, since the trails are mostly unoriented and seldom cut into the authigenic part of the quartz grains. However, the inclusions are commonly excellent for microthermometry analysis, used as a supplement to the less abundant petroleum inclusions in authigenic quartz. Petroleum inclusions can also commonly be observed in detrital feldspars, as they dissolve to form kaolinite or secondary

porosity (Fig. 4A and B). These inclusions have a qualitative value for the diagenetic time aspect, but cannot be used for microthermometry due to poor sealing. Texturally, poor sealing is shown by very ragged shape of the inclusions and variations in both fluorescence and the proportions between liquid and vapour (Fig. 4B). Quartz diagenesis is one of the most effective mechanisms of reducing the reservoir quality. Petroleum inclusions in authigenic quartz are of particular interest for the relative timing between petroleum reservoir filling and quartz diagenesis. Fig. 5 shows contrasting examples of this, respectively, early presence of petroleum shown as inclusions in the dust rim of the quartz and recent reservoir filling with formation of quartz overgrowths prior to entrapment of petroleum inclusions.

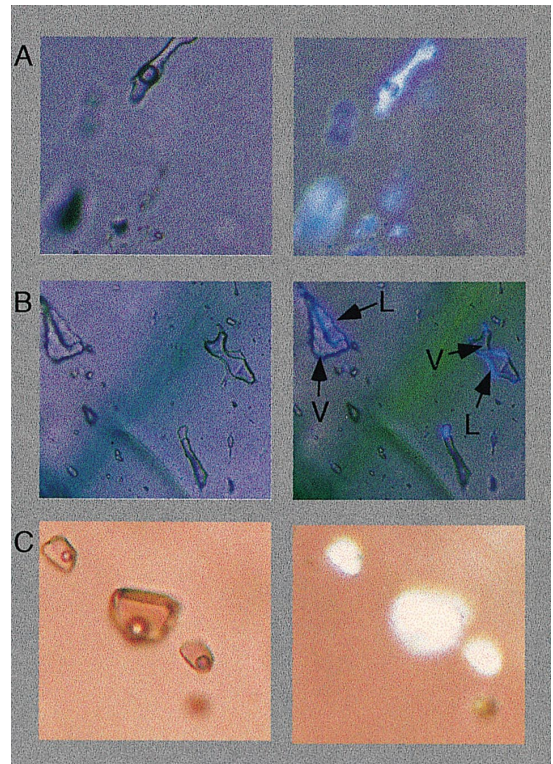


Fig. 3. The colour, fluorescence colour and the proportion between liquid and vapour at room temperature can be used for identification of petroleum inclusions and for a quick qualitative indication of fluid composition (see text for further explanation). (Left side = transmittant light only, right side = transmittant and UV light).

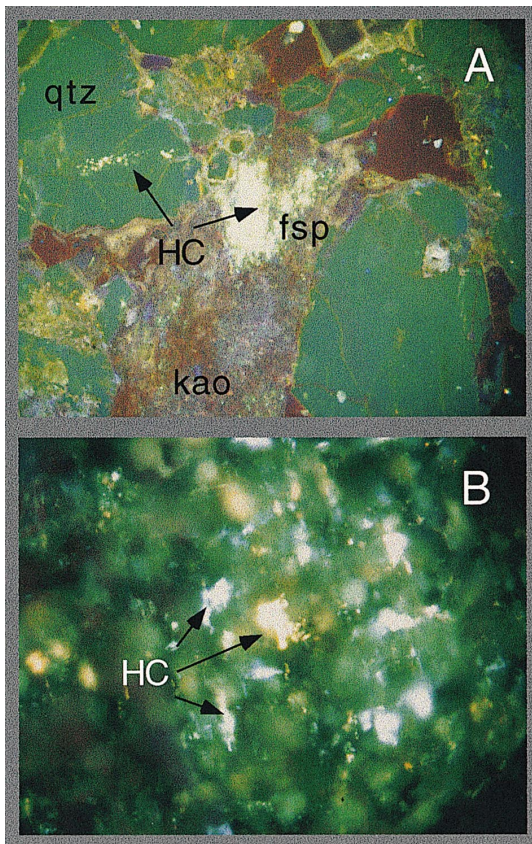


Fig. 4. Microphotos of petroleum inclusions in sandstones. (both photos = UV light only). (A) Petroleum inclusions occur both in detrital quartz and feldspar. The feldspar shows alteration to kaolinite. The abundance of petroleum inclusions in the feldspar is very high. (B) An enlargement of the feldspar shows very ragged shapes and variable fluorescence colours of the petroleum inclusions. This indicates that the inclusions are not properly sealed and cannot be recommended for microthermometry analysis.

Petroleum inclusions may also occur in mineralised fractures both in chalk and in clastic reservoirs. Examples of petroleum inclusions in primary growth zones in fracture minerals (Fig. 6) give evidence for the presence of petroleum at the time of fracture cementation, and suggest that the fractures were conduits for petroleum migration.

4.3. Microthermometry

Microthermometry analysis of petroleum inclusions follows the general procedure outlined by

Shepherd et al. (1985). Selection of inclusions for analysis should be based on a critical evaluation of textures. Inclusions that show textural indications of poor sealing or post-entrapment changes should be avoided. Microthermometry of petroleum inclusions in quartz, carbonates and barite usually gives reproducible results. Petroleum inclusions trapped in partly dissolved K-feldspars often show extreme variations in size of the vapour bubble, very irregular shapes and variable fluorescence, which indicate poor sealing, and are not recommended for microthermometry. Leakage or decrepitation of inclusions may occur during analysis, and need thorough attention of the operator and checks on the reproducibility. The best sequence in the laboratory is to measure the homogenisation before the low temperature phase transitions. It is important to start with the populations of inclusions, which homogenise at lower temperatures before proceeding to homogenisation measurements at higher temperatures. This mostly means that all measurements of homogenisation temperatures for petroleum inclusions should be finished before measurements of aqueous inclusions. Freezing of ice in the aqueous inclusions very often creates microcracks in diagenetic minerals like carbonates and barite, and this may lead to severe leakage of inclusions. Ice melting temperatures should therefore be the last analysis in the sequence.

The most useful phase transition for petroleum inclusions is the homogenisation. The homogenisation behaviour gives certain constraints on the two-phase envelope. Liquid and vapour homogenisations are both common, and critical homogenisation may also occur. For vapour homogenisation, the homogenisation temperature represents an absolute maximum for the critical point. Likewise, for liquid homogenisation, the homogenisation temperature represents an absolute minimum for the critical point. In order to use the homogenisation temperature quantitatively for calculation of isochores and estimation of trapping conditions, additional information on petroleum fluid composition and microthermometry from coexisting aqueous fluids are necessary. The methodology of this will be discussed later.

If fluorescence microscopy is not available, the low temperature behaviour can be used to distinguish aqueous and petroleum inclusions. Aqueous inclusions freeze into ice and hydrates, and consist only

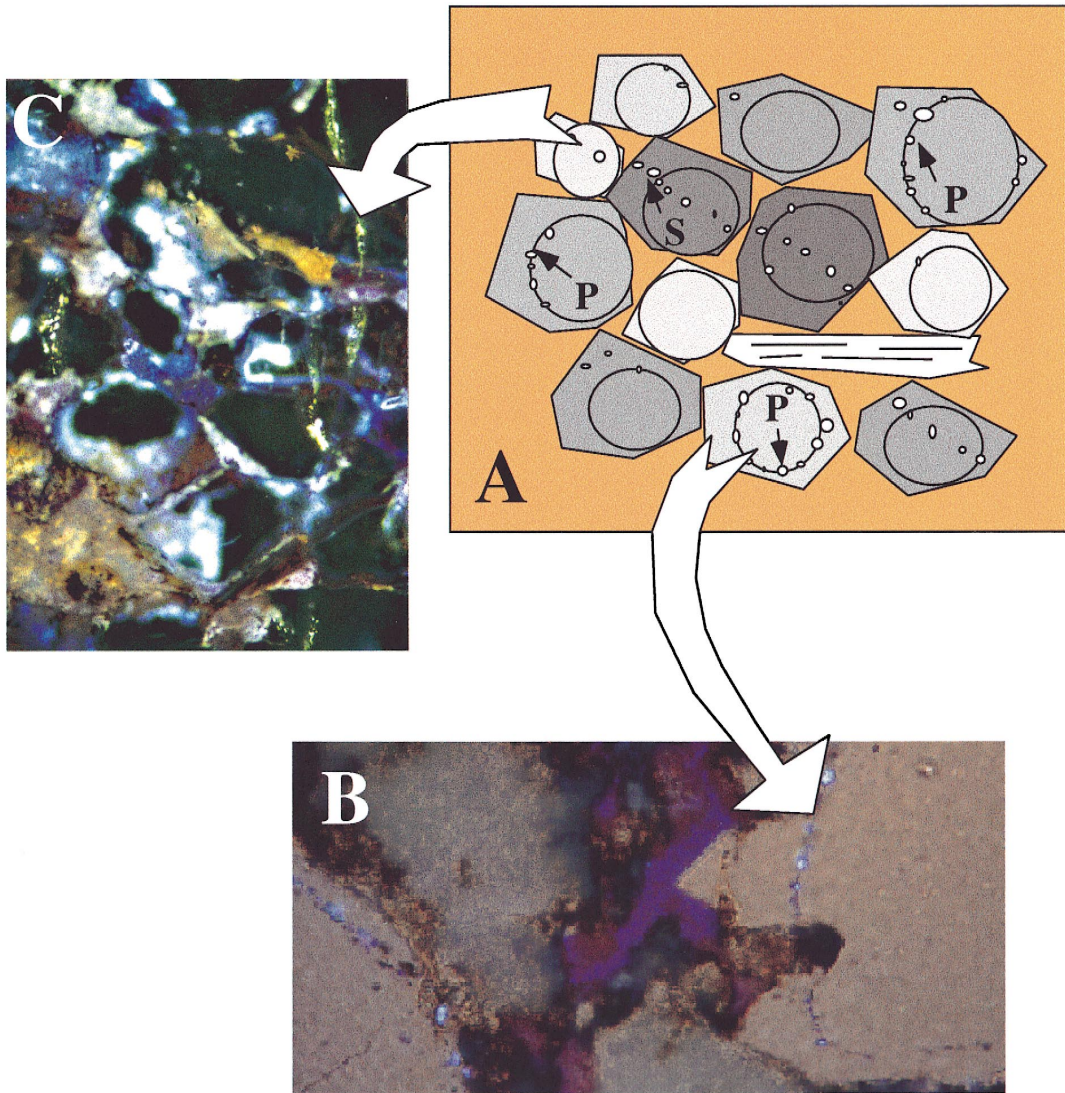


Fig. 5. (A) Textural relationships between petroleum inclusions and quartz in sandstones can be used as a dating tool. Occurrence of petroleum inclusions in the dust rim of quartz overgrowths (marked with P) shows that petroleum was present at the time of quartz diagenesis. Secondary trails of petroleum inclusions (marked with S) cutting both the detrital and the authigenic part of the quartz grains indicate that trapping of these inclusions occurred after the main phase of quartz diagenesis. The two microphotographs show examples of the principles in the illustration. They present different reservoirs, which experienced respectively an early (B; UV and transmittent light) and a recent reservoir filling (C; UV light only).

of solids and a vapour phase at low temperature. The liquid appears again at the eutectic point during heating, typically around -50°C (assuming a pseudoternary $\text{H}_2\text{O}-\text{NaCl}-\text{CaCl}_2$ system). Although freezing of a solid (wax) may take place in petroleum

inclusions at low temperature depending on the composition, it will generally not be possible to freeze the total amount of liquid into solids as can be done for aqueous inclusions. The low temperature behaviour of petroleum inclusions has, however, been

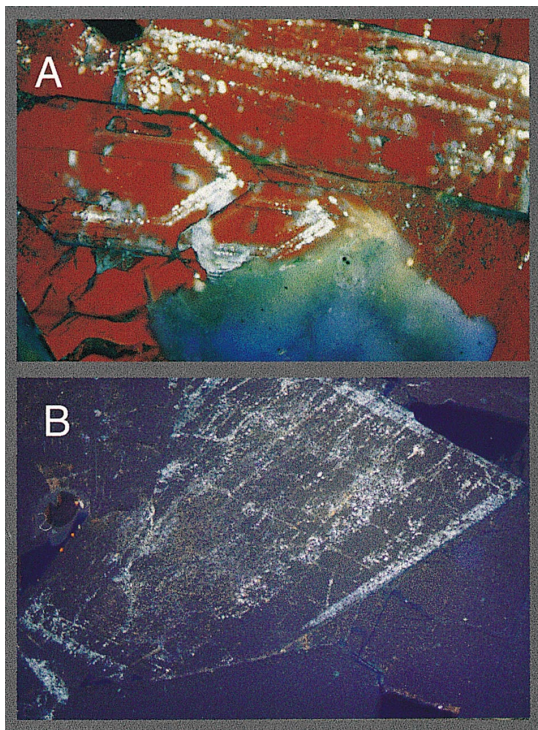


Fig. 6. Two examples of primary petroleum inclusions in fracture fillings. (A) A fracture filling of barite in chalk from the North Sea (transmittent and UV light). (B) A carbonate fracture filling in limestone from the Barents Sea (UV light only).

little investigated. It is a very cumbersome method of distinguishing aqueous and petroleum inclusions, and is presently of little quantitative use.

Another phase transition that may occur in petroleum inclusions is the melting of clathrate. This phase transition will always be possible to observe if an aqueous phase is visible in the inclusions, and may also occasionally be observed in inclusions without a visible aqueous phase. However, the clathrate melting temperatures have so far found little quantitative use.

4.4. Fluorescence spectroscopy

Excitation by UV light causes petroleum fluids to emit light (or fluoresce) in the visible range (400–700 nm). The fluorescence emission of organic molecules is due to electronic transitions involving carbon–carbon double bonds. The part of a molecule, which can be excited by incident light, is called a chromophore. The analytical set up of fluorescence mi-

croscopy has been described in detail by Burruss (1991). A high-pressure mercury lamp is often used as an excitation source. Monochromatic light can be generated by use of bandpass filters, and the most commonly used excitation wavelength for petroleum is 365 nm. The monochromatic UV light is directed onto the sample and the emitted light is transmitted from the microscope into a spectrograph and detector system. Different combinations of optical components (e.g. filters, lenses, beam splitters, fibre optics) may be used (Burruss, 1991; Guilhaumou et al., 1990; Kihle, 1995). The efficiency of transmission is highly dependent on these components, and absorption in the light path may lead to significantly enhanced detection limits. This can especially be problematic in the deep blue range (400–450 nm). Optical components may also emit fluorescence, leading to undesired contamination. The analysis therefore requires thorough knowledge of the specific optical components used in the light path. The method requires calibration both of wavelengths and intensity. If only relative intensities are used, the only intensity calibration necessary is a check of linear response. Absolute intensities are not of major interest for fluid inclusion studies, due to dependency on factors, such as inclusion size and geometry and depth in the sample.

Various parameters have been used to quantitatively describe the fluorescence emission spectrum (Fig. 7). λ_{\max} is the wavelength of maximum intensity. Different types of colourimetric quotients have been used: a QF-535 factor was defined as the ratio of the 535–750 nm flux to the 430–535 flux (Pradier et al., 1990; Guilhaumou et al., 1990), and a $Q_{650/500}$ factor was defined as ratio of the intensity at 650 nm to the intensity at 500 nm (Hagemann and Hollerbach, 1986; Stasiuk and Snowdon, 1997).

The relationship between fluorescence and chemical composition of the petroleum is highly complex. The main fluorescing components in petroleum are aromatic hydrocarbons (Hagemann and Hollerbach, 1986; Khavari Khorasani, 1987). NSO compounds show a less intensive fluorescence at higher wavelengths than the aromatic compounds in the red range (Khavari Khorasani, 1987). Khavari Khorasani (1987) also showed fluorescence from the saturated fraction of petroleum with intensity maxima at low wavelengths in the blue–green range. The fluores-

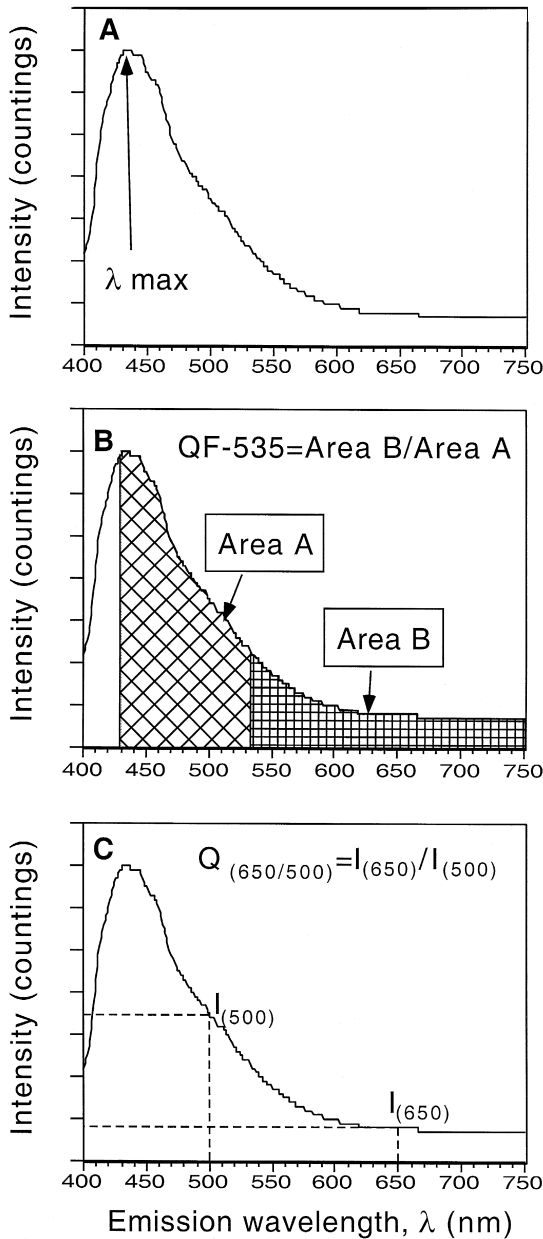


Fig. 7. Definitions of fluorescence emission parameters. (A) The wavelength of maximum intensity, λ_{\max} . (B) The QF-535 factor. (C) The $Q_{650/500}$ factor.

cence of the saturated fraction is, however, most probably caused by contamination of minute quantities of aromatic hydrocarbons. Interpretation of fluorescence emission spectra is also complicated by

intra- and intermolecular interactions (Bertrand et al., 1986). A number of processes may occur (Bertrand et al., 1986): high concentrations of chromophores may lead to absorption of emitted fluorescence; other matrix molecules may absorb both exciting and emitting fluorescence and the emission spectra may be displaced due to interactions. Thus, individual compounds in petroleum cannot be identified by fluorescence spectroscopy. The fluorescence emission represents, however, a very important fingerprint on composition. A correlation between fluorescence and bulk fluid properties, such as API gravity has been shown (e.g. Stasiuk and Snowdon, 1997). The API gravity has been defined as $^{\circ}\text{API} = (141.5/S_0) - 131.5$, where S_0 is the stock tank oil specific gravity.

The heavy oils show fluorescence emission at higher wavelengths than lighter oils. Due to the highly complex relationship between fluorescence and fluid composition, empirical calibrations between fluorescence properties and API gravity probably work best for genetically related petroleum fluids and should not be used as a universal valid calibration. Fluorescence spectroscopy is especially a valuable tool used to distinguish different generations of inclusions (Guilhaumou et al., 1990). Since it is a microscopic technique, the results can be correlated on a one-to-one basis with microthermometry. This provides a possibility to check if a variation in homogenisation temperatures is related to differences in composition or trapping conditions.

4.5. Other spectroscopic methods

Several other spectroscopic methods have been tested on petroleum inclusions, but so far, none of these methods have found extensive use.

Synchronous fluorescence excitation-emission spectroscopy represents a variety of the fluorescence spectroscopy described above. Instead of monochromatic excitation at constant wavelength, a continuous light source is used (e.g. a xenon burner), and synchronous scanning of excitation and emission wavelengths is done at a fixed difference between the monochromators (Kihle 1995; Musgrave et al., 1994). The method shows an ability of recognising differences between inclusions with similar fluorescence characteristics at constant excitation (Kihle, 1995), and may thus be important as a fingerprinting tool in

correlation studies. However, the relationship to composition is still obscure.

Raman and Fourier-transform infrared spectroscopy detect transitions between vibrational energy levels (Pironon and Barres, 1990; Wopenka et al., 1990). A monochromatic laser light source in the visible range (e.g. 514.5 nm) is used for Raman spectroscopy, and the measured spectrum results from inelastic (Raman) scattering of the incident light. The method has proven to be very useful for N_2 - CO_2 - CH_4 fluids, and is described in more detail by Burke (2001). For petroleum inclusions, however, Raman spectroscopy is severely hampered by fluorescence emission, which is orders of magnitude higher than the Raman scattering (Wopenka et al., 1990; Pironon et al., 1990). Pironon et al. (1990) tried to avoid this problem by using a laser source in the near-infrared range (i.e. 1064 nm), but most of the fluorescent inclusions during visible Raman spectroscopy were also fluorescent in the near-infrared range.

Fourier-transform infrared spectroscopy is based on absorption of the incident light, and a polychromatic excitation source in the 1100–2000 nm range is used (Wopenka et al., 1990). The method has stringent requirements for the minimum size of the inclusion, the type of host mineral and sample preparation (Wopenka et al., 1990). Functional groups ($-CH_2$, $-CH_3$) can be identified from the infrared absorption frequencies. Quantitative estimates of the $-CH_2$: $-CH_3$ abundance based on peak areas may give an indication of the average alkane chain length (Pironon and Barres, 1990). Calibration of the method shows significant differences between mobile fluid standards and synthetic fluid inclusions with the same composition (Pironon and Barres, 1990). A spectral deformation, involving the shape, but not the peak position, of the synthetic fluid inclusions was observed for pure *n*-alkane compositions. The method is also sensitive to internal pressure in the inclusion (Barres et al., 1987).

Nuclear magnetic resonance (1H NMR) has also been tested on petroleum inclusions (Dereppe et al., 1994). The technique is based on electron spin. It can only be used for analysis of bulk samples. Volumetric ratios between water and oil, paraffinic and aromatic compounds, CH_2 and CH_3 of the paraffinic chain can be estimated (Dereppe et al., 1994).

4.6. Volumetric measurements

Confocal laser scanning microscopy has recently been used for determination of the volumetric ratio between liquid and vapour in petroleum inclusions at room temperature (Pironon et al., 1998; Aplin et al., 1999). The laser causes fluorescence in the liquid, but not in the vapour of the inclusion. The two phases can thus readily be distinguished. The analytical concept of the microscope is based on filtering of emission light by a confocal pinhole (Pironon et al., 1998). This allows a very precise focussing within the sample. The analysis is done by locating the top and bottom of the inclusion by visual observation. Scans are then made at approximately 1 μm steps through the inclusion (Aplin et al., 1999). A series of two-dimensional images is produced. A three-dimensional model of the inclusion can be reconstructed from the series of two-dimensional images by using a visualisation tool (Pironon et al., 1998).

The capability of this analytical technique is the determination of the total volume of the inclusion and the volumetric ratio between liquid and vapour. In order to determine the molar volume, however, additional information on fluid composition and the average molecular weight is necessary.

5. Destructive analytical methods

For comprehensive compositional data the sample must be crushed. The methods used comprise gas chromatography (GC), gas chromatography-mass spectrometry (GC-MS) and gas chromatography-initial ratio mass spectrometry (GC-IRMS). There are two main problems of destructive analytical methods, which have been of concern: (1) if more than one generation of petroleum fluid inclusions are present, the composition will represent a mixture; (2) the analyses can be contaminated by residues of the present-day fluid adsorbed on the mineral surface. A thorough purification procedure is therefore required. The purification procedures can consist of: Soxhlet extraction with a mixture of dichloromethane and methanol; rinsing in chromic acid and rinsing in hydrogen peroxide (Karlsen et al., 1993; George et al., 1997). This section deals with the general aspects of destructive analyses of petroleum inclusion fluids,

and discusses how the two problems above can be reduced.

Compositional analysis of petroleum inclusion fluids presents a challenge both due to phase separation and to the small and somewhat unpredictable amounts of fluid in the sample. Two different basic approaches can be used.

5.1. Off-line crushing

Off-line crushing has been used in combination with GC and GC-MS (Karlsen et al., 1993; Kihle et al., 1995; George et al., 1997) and GC-IRMS (Andresen et al., 1998). The phase separation is a serious problem for this approach. The gas and the liquid fraction must be analysed separately on different aliquots. The amount of sample needed for this approach is typically of the order 10–20 g. Hand-picking of these large amounts of sample is practically impossible. Some improvement of sample material can, however, be achieved by separation techniques, such as sieving. The fine-grained fraction generally has low abundance of fluid inclusions and large grain surface areas. Removal of the fine-grained fraction will thus tend to (1) increase the amount of fluid per gram of sample and (2) reduce contamination problems with surface coatings.

For analysis of the gas fraction, a crushing cell that can be evacuated after insertion of the sample,

must be used (Karlsen et al., 1993; Kihle et al., 1995). When the cell has been pumped down to vacuum, the sample can be crushed, and the inclusion gas can be withdrawn by a syringe through a septum. In order to avoid adsorption on mineral surfaces and chamber walls, the cell needs heating to approximately 90°C.

Analysis of the liquid fraction does not necessarily require vacuum. Crushing can be done in a mortar under a solvent, such as dichloromethane (Karlsen et al., 1993). This will, however, result in a loss of the light hydrocarbons, i.e. < C₁₅.

Since the amounts of total fluid in the aliquots are variable, due to different fluid inclusion abundances, recombination of the two fractions becomes difficult. Recombination can, however, be done, if both fractions are analysed in the same aliquot of sample and the total gas volume in the crushing cell is quantified by use of a separation line (Kihle et al., 1995). The method has, however, serious problems with high detection limits of the liquid fraction.

5.2. On-line crushing

A method for on-line crushing and analysis using a GC with a modified injector was described by Burruss (1987). This modification allows crushing of the sample in the injector, and the fluid released during crushing is swept into the GC with the carrier

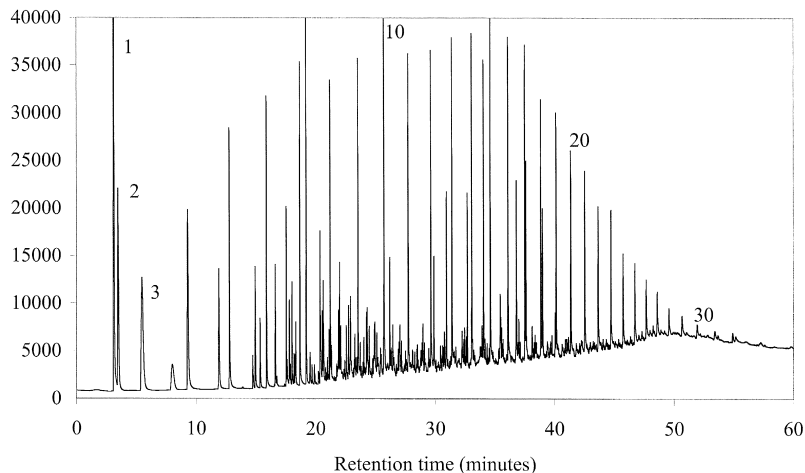


Fig. 8. On-line gas chromatography results for petroleum inclusions in fracture cement from the North Sea. Identification of some *n*-alkanes is shown by the numbers.

gas. The requirement for sample is typically of the order of 20–40 mg. Hand-picking of samples prior to analysis, using a UV microscope, ensures a sufficient fluid inclusion abundance, and as far as possible, separation of different fluid inclusion populations. The problems with mixing of different fluid inclusion generations are therefore minimised.

The results show a compositional range from C_1 to C_{30} , with no phase separation problems (Fig. 8). Separation between C_1 and C_2 can be obtained, and the majority of individual components up to C_7 can be identified and quantified. The method shows clearly best results for fracture cement samples. The fluid content in fracture cements is generally 2–3 times higher than in sandstones (Munz et al., 1999b), and the method is therefore best suited for fractured reservoirs, such as chalk and limestone reservoirs.

6. Applications

6.1. Fluid correlation in space and time

Mapping of petroleum compositional characteristics has been a commonly used tool for determination of fluid transport directions. Biomarkers and maturity parameters in the range C_{19} – C_{35} have been central in fluid correlation studies. These compounds have the advantage that their origin, in terms of the biological link and thermal behaviour, has been the focus of extensive research (e.g. Mackenzie, 1984). They are therefore useful for correlation of oils with each other and with their proposed source rocks and for assessment of their thermal maturity (Mackenzie, 1984). Biomarkers and maturity parameters occur, however, only as trace components in oils, and the technique is therefore not suited when fluids of condensate or wet gas composition are involved. The samples used for such studies include DST samples and core extracts. Core extracts are obtained by extraction with organic solvents and may include immobile phases, such as tar mats and adsorbed reservoir surface coatings, extracts of indigenous organic matter in addition to the remains of the reservoir fluids (Larter and Aplin, 1995). The content of NSO compounds is commonly higher in core extracts than in DST oils (Leythaeuser and Rückheim, 1989; Horstad et al., 1990; Stoddart et al., 1995;

Larter and Aplin, 1995; Baylis, 1998). Direct comparison between data from the two types of samples is therefore problematic and needs specific consideration.

A growing body of literature shows that gasoline range (C_4 – C_{12}) compounds can also be used for fluid correlation (e.g. Ten Haven, 1996; Odden, 1999; Odden et al. 1998). The origin of the gasoline range compounds is less understood (Mango, 1997), and a direct relationship to biological precursors cannot be shown. The gasoline compounds have, however, the advantage of being abundant in all types of petroleum fluids. The method is especially useful for condensate compositions or even wet gas. Only DST samples can be used for this type of study, since core extracts show a loss of light hydrocarbons ($< C_{15}$).

Until recently, fluid correlation has been limited to the spatial distribution of present-day petroleum. The development of analytical methods of petroleum in fluid inclusions opens for fluid correlation also in time. Biomarkers and maturity parameters can be obtained from methods using off-line crushing. Comparison between data from present-day fluids and fluid inclusions may establish compositional differences in both time and space. This has led to the recognition of early charge histories with both lower maturity and different sources involved (Karlsen et al., 1993; Lisk et al., 1996; George et al., 1996, 1997, 1998). On-line GC analysis of petroleum inclusion fluids is a suitable technique for determination of gasoline range compounds, but has so far not been used in correlation studies. With the increasing interest in gasoline range compounds in general, it is likely that this technique will be a valuable tool in the future.

6.2. PVT characterisation

An important objective of most fluid inclusion studies is to calculate fluid densities and isochores, and to estimate the pressure and temperature conditions of trapping, either by combining information from solids or from coexisting fluid phases. For petroleum inclusions, it may also be of great interest to estimate fluid properties at pressure and temperature conditions other than the trapping conditions. This may include saturation pressure at specified temperature or the gas-to-oil ratio (GOR) at any

specified pressure and temperature. These calculations are all done using an equation of state. The most accurate results for complex petroleum fluids can be obtained by two- or three-constant, cubic equations (Firoozabadi, 1988). Among the most used cubic equation of state are the Soave–Redlich–Kwong and the Peng–Robinson equations of state (Soave, 1972; Peng and Robinson, 1976; Robinson and Peng, 1978). For accurate estimation of saturated liquid volume, these equations may need some adjustment (Péneloux et al., 1982). Commercial software, which is used in reservoir engineering, may also be applied to fluid inclusion studies, although this usually involves some more effort from the user. In Sections 6.2.1 and 6.2.2, calculation of two-phase envelopes and pressure–temperature conditions of trapping is addressed. For a more extensive review of PVT modelling, the textbooks of Pedersen et al. (1989) and Danesh (1998) can be recommended.

6.2.1. Two-phase envelopes and isochores

The required input for calculation of two-phase envelopes using an equation of state is the total fluid composition in mole percent. In addition, the critical properties of each component must be characterised, and binary interaction coefficients between the different components must be known. For isochore calculation, the homogenisation temperature is also necessary.

The most problematic point of the PVT modelling is characterisation of the fluid composition. Reservoir petroleum fluids normally contain hundreds of different components. To treat all components separately is impossible, from either an analytical or a computational view. Components with similar physical characteristics are instead grouped together as pseudocomponents. This is commonly done by treating N_2 , CO_2 and each hydrocarbon compound between C_1 and C_5 individually, and dividing the C_{6+} components into boiling point fractions. The classical method for separation of oil into boiling point fractions and a heavy molecular residue has been distillation. Each fraction covers the range from $0.5^\circ C$ above the previous n -paraffins to $0.5^\circ C$ above the carbon number used to identify the group (Katz and Firoozabadi, 1978). Boiling point fractions can also be called single-carbon-number groups (Whitson, 1983). Molecular weights and density (usually at

atmospheric pressure and $60^\circ F/15^\circ C$) can be determined by analysis of each boiling point fraction and the residue. A review of the analytical methods for these determinations is given by Pedersen et al. (1989). The distillation procedure may be replaced by GC (Osjord et al., 1985). The procedure still requires determination of molecular weight and density of the residue. Critical properties for the pseudo-components (i.e. single-carbon-number groups and the residue) can be derived from the molecular weights and densities by various correlation schemes (e.g. Kesler and Lee, 1976; Riazi and Daubert, 1987).

Although analysis of petroleum inclusions has made enormous progress for the last decade, as described in the previous sections, sufficient information on the composition of petroleum inclusion fluids for PVT modelling is still problematic to obtain. Isochores have been calculated by combining microthermometry data with compositional data of present-day, mobile hydrocarbon fluids (e.g. Narr and Burruss, 1984; McLimans, 1987; Bodnar, 1990; Munz et al., 1999a). This is, however, only a valid approach for cases with recent reservoir filling where the composition of the inclusion fluid is approximately the same as the present-day reservoir fluid.

Problems arise with this method when the composition of the inclusion fluid is not identical to the present-day reservoir fluid. This can partly be solved by an iterative approach (Aplin et al., 1999). A ‘model’ composition of the inclusions is calculated by using the present-day reservoir fluid composition as a regression parameter. The necessary data from fluid inclusion analyses are microthermometry and the volumetric ratio between vapour and liquid at room temperature, determined by confocal laser scanning microscopy. The calculations are done as a series of iterations, titrating gas components (C_1 – C_5) into or out of the fluid composition, until a composition is found that matches the volumetric constraints at room temperature (experimental) and at the homogenisation temperature (calculated). The accuracy of this method is dependent on the initial composition. Aplin et al. (1999) assume that the inclusion fluid is most accurately modelled if the fluid, which is used as input for the calculations, is genetically related.

A procedure for compositional characterisation of inclusion petroleum, based on on-line GC, was sug-

gested by Munz et al. (1999b). It is similar to the procedure used for present-day fluids in reservoir engineering. Compounds in the range from C_1 to C_5 were treated as individual components. The range from C_6 to C_{30+} was divided into pseudocomponents, by integrating ranges instead of peaks. Pseudocomponents were defined as single-carbon-number groups, and the average values from the literature for the critical properties of these pseudocomponents were used. The properties of the residue were estimated by extrapolation of the distribution of components in the range C_{8-10} – C_{30} .

The compositional characterisation described by Munz et al. (1999b) could be used as input data to the method of Aplin et al. (1999). However, this may need some adjustment of the software. The GC analyses show high precision for the gas components, but more problems for the heavy end. A more accurate result may therefore be obtained by using the properties of the heavy components as a tuning parameter, rather than the gas content.

6.2.2. *Interpretation of coexisting aqueous and petroleum fluid systems*

Petroleum always coexists with an aqueous fluid phase in sedimentary basins. Even in reservoirs with high petroleum saturation, the formation water cannot be entirely displaced. Fluid immiscibility relationships must therefore be considered.

In the methods described above, solubility of water in petroleum has been disregarded. Two arguments may justify this (Munz et al., 1999b): (1) the solubility of water in petroleum is very small; (2) the properties of water would not be significantly different from the more polar compounds of petroleum. Given the problems of describing the heavy end of petroleum, omission of the very small amounts of dissolved water will not significantly affect the results. The solubility of petroleum compounds in water is also low, but cannot be disregarded. The highest solubilities are found for methane and the light aromatics. The properties of methane are significantly different from water. Dissolved methane in water may therefore change the PVT properties of the aqueous fluid (Hanor, 1980), and needs to be considered in estimation of trapping pressure and temperature conditions.

The pressure and temperature conditions for trapping of two coexisting fluid phases with no mutual solubility can be estimated by the intersecting isochore principle (Roedder and Bodnar, 1980). For two fluids with a mutual solubility, however, the criterion for immiscibility is equal homogenisation temperature, where the low density fluid homogenises to the vapour phase and the high density fluid to the liquid phase (Roedder, 1984; p. 256). Ideally, coexisting petroleum and aqueous inclusions should therefore show the same homogenisation temperature. Numerous examples show that petroleum inclusions typically homogenise at lower temperature than the coexisting aqueous inclusions (e.g. Nedkvitne et al., 1993; Munz et al., 1998, 1999a). The reason for this is that the mutual solubility is too small to be observed by microthermometry. The analysed homogenisation of aqueous inclusions represents the final homogenisation. Phase transitions (e.g. partial homogenisation, clathrate melting) related to dissolved methane should take place at low temperature, but are commonly difficult to observe. The homogenisation of petroleum inclusions, however, represents only a partial homogenisation. The final homogenisation would have been dissolution of the aqueous phase into the then single-phase petroleum. But again, due to the extremely small amounts of water, this phase transition has not been reported. Observations of an aqueous fluid within the petroleum inclusions generally relate to heterogeneous trapping. Final homogenisation temperature does, therefore, not have any relevance and cannot, in most cases, be measured without decrepitation. Immiscibility is therefore difficult to show from the microthermometry, and recognition of equilibrated, coexisting petroleum and aqueous inclusions must rely on textural criteria only. If textural criteria indicate contemporaneous trapping of petroleum and aqueous inclusions, methane saturation of the aqueous inclusions can be assumed, and the aqueous homogenisation temperature represents the trapping temperature for both types of inclusions (Nedkvitne et al., 1993). The trapping pressure may then be found by intersection between the petroleum inclusion isochore and the trapping temperature (Fig. 9).

Petroleum fluids may also experience phase separation at geological conditions. A situation with three immiscible fluid phases (gas, oil, water) will be the

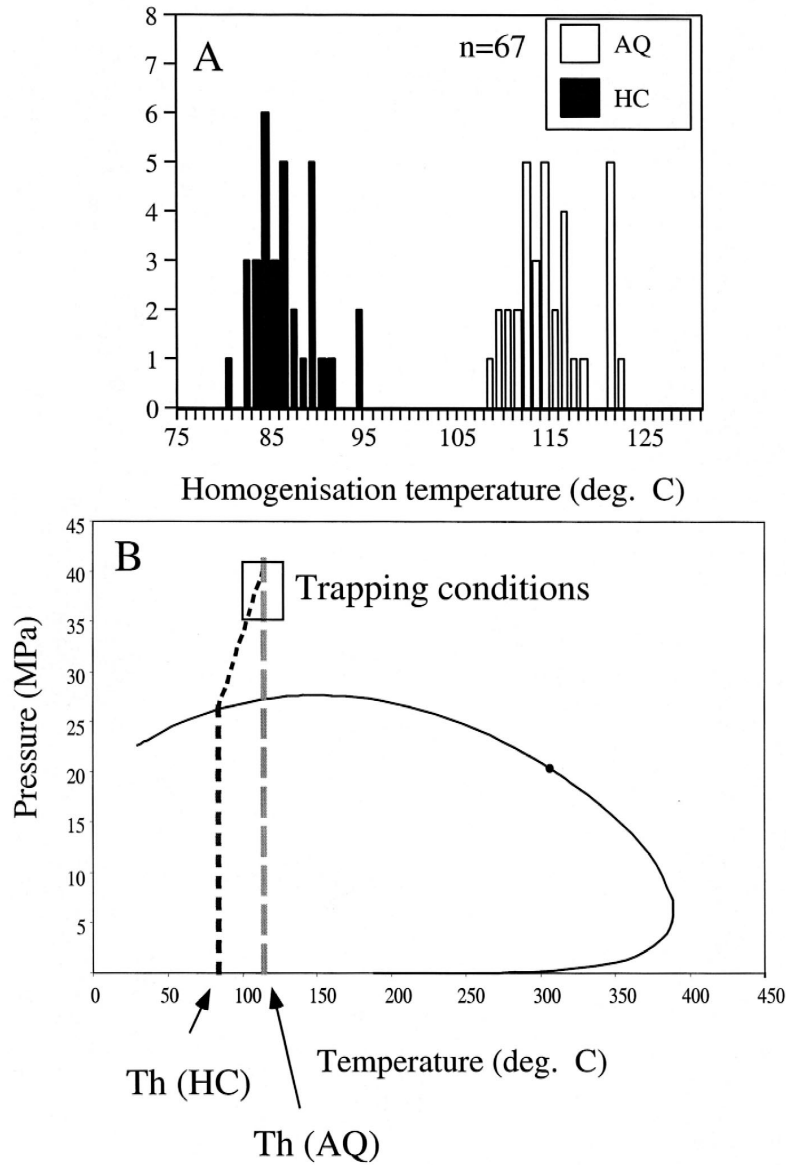


Fig. 9. Coexisting aqueous (AQ) and petroleum (HC) inclusions. (A) Microthermometry results. (B) On-line gas chromatography results (not shown) can be used for constructing the two-phase envelope. The trapping conditions for both types of inclusions can be estimated by combining GC results and the microthermometry results in A. The homogenisation temperature of the aqueous inclusions (approximately 115°C) represents the trapping temperature of both fluids. The pressure can be found from the intersection with the isochore for the petroleum inclusions.

consequence of phase separation, and again, this should be recognised by equal homogenisation temperatures. Munz et al. (1999a) showed that the difference in homogenisation temperature between cogenetic aqueous and petroleum inclusions is an

important qualitative indicator for the degree of undersaturation of the petroleum inclusions (oil or gas). In a situation where an undersaturated oil gets saturated with gas, the homogenisation temperature will approach the homogenisation temperature of the co-

existing aqueous inclusions. A case study from the Frøy and Rind fields in the North Sea showed that the difference in homogenisation temperatures between recently trapped aqueous and petroleum inclusions corresponded to differences in PVT results for the DST fluid samples, and could be used for detection of compartmentalisation (Munz et al., 1999a). This can be a very useful tool in evaluation of fault properties.

7. Conclusion

Analysis of petroleum inclusions and the application to exploration and reservoir appraisal have experienced rapid development during the last decade.

The traditional correlation studies may now also include fluid inclusion data. The analytical development enables characterisation of maturity and source facies of petroleum inclusion fluids, which can be used together with data on DST fluid samples and core extracts. This has led to recognition of early charge histories with both lower maturity and different sources involved (Karlsen et al., 1993; Lisk et al., 1996; George et al., 1996, 1997, 1998).

The development has also been directed towards an improved understanding of the physical properties of petroleum inclusion fluids by including microthermometry, volumetric measurements by confocal laser scanning microscopy and chemical data in PVT modelling (Aplin et al., 1999; Munz et al., 1999b). Although these methods are in their early stages concerning precision and accuracy, data necessary for fluid flow modelling, such as fluid densities, viscosities, pressure and temperature, can be estimated. Numerical modelling of reservoir filling histories, such as the models of England (1989), England and Mackenzie (1989) and England et al. (1987, 1995), can therefore be constrained by analytical data from fluid inclusions.

Integration of fluid inclusion data and present-day fluid samples can thus give a significantly improved resolution on fluid distributions and properties in time and space.

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References

- Andresen, B., Munz, I.A., Johansen, H., Johansen, I., 1998. Compositional and isotope data on hydrocarbon fluid inclusions — a tool for better understanding of light hydrocarbon migration and trapping. 215th American Chemical Society National Meeting, Dallas March 29–April 2. (abstr.).
- Aplin, A.C., Macleod, G., Larter, S.R., Pedersen, K.S., Sørensen, H., Booth, T., 1999. Combined use of confocal laser scanning microscopy and PVT simulation for estimating the composition and physical properties of petroleum in fluid inclusions. *Mar. Pet. Geol.* 16, 97–110.
- Barres, O., Burneau, A., Dubessy, J., Pagel, M., 1987. Application of micro-FT-IR spectroscopy to individual hydrocarbon fluid inclusion analysis. *Appl. Spectrosc.* 41, 1000–1008.
- Baylis, S.A., 1998. Geochemical comparison of core extracts and oil samples in reservoir. *Org. Geochem.* 29, 463–484.
- Bertrand, P., Pittion, J.-L., Bernaud, C., 1986. Fluorescence of sedimentary organic matter in relation to its chemical composition. *Org. Geochem.* 10, 641–647.
- Bodnar, R.J., 1990. Petroleum migration in the Miocene Monterey Formation, California, USA: constraints from fluid-inclusion studies. *Min. Mag.* 54, 295–304.
- Burke, E.A.J., 2001. Raman microspectrometry of fluid inclusions. *Lithos* 55, 139–158 (this volume).
- Burruss, R.C., 1981. Hydrocarbon fluid inclusions in studies of sedimentary diagenesis. In: Hollister, L.S., Crawford, M.L. (Eds.), *Short Course in Fluid Inclusions: Applications to Petrology*. Mineral. Assoc. Canada, vol. 6, pp. 138–156.
- Burruss, R.C., 1987. Crushing cell, capillary column gas chromatography of petroleum inclusions: method and application to petroleum source beds, reservoirs and low hydrothermal ores. In: Roedder, E., Kozłowski, A. (Eds.), *Fluid Inclusion Research* 20, p. 59, (abstr.).
- Burruss, R.C., 1991. Practical aspects of fluorescence microscopy of petroleum fluid inclusions. Luminescence microscopy and spectroscopy: Qualitative and quantitative applications. In: Barker, C.E., Kopp, O.C. (Eds.), *SEPM Short Course* 25, pp. 1–7.
- Burruss, R.C., Cerone, K.R., Harris, P.M., 1983. Fluid inclusion petrography and tectonic-burial of the Al Ali No 2 well: Evidence for the timing of diagenesis and oil migration, northern Oman Foredeep. *Geology* 11, 567–570.
- Danesh, A., 1994. PVT and phase behaviour of petroleum fluids, *Developments in Petroleum Science* 47 Elsevier, 387 pp.
- Dereppe, J.-M., Pironon, J., Moreaux, C., 1994. Characterization

- of the composition of fluid inclusions in minerals by ^1H NMR. *Am. Min.* 79, 712–718.
- England, W.A., 1989. The organic geochemistry of petroleum reservoirs. *Org. Geochem.* 16, 415–425.
- England, W.A., Mackenzie, A.S., 1989. Some aspects of the organic geochemistry of petroleum fluids. *Geol. Rundsch.* 78, 291–303.
- England, W.A., Mackenzie, A.S., Mann, D.M., Quigley, T.M., 1987. The movement and entrapment of petroleum fluids in the subsurface. *J. Geol. Soc. (London)* 144, 327–347.
- England, W.A., Muggerridge, A.H., Clifford, P.J., Tang, Z., 1995. Modelling density-driven mixing rates in petroleum reservoirs on geological time-scales, with application to the detection of barriers in the Forties Field (UKCS). In: Cubitt, J.M., England, W.A. (Eds.), *The Geochemistry of Reservoirs* 86 Geol. Soc. London Spec. Publ., pp. 185–201.
- Firoozabadi, A., 1988. Reservoir-fluid phase behavior and volumetric prediction with equation of state. *JPT*, 397–406.
- George, S.C., Krieger, F.W., Eadington, P.J., Quezada, R.A., Greenwood, P.F., Eisenberg, L.I., Hamilton, P.J., Wilson, M., 1997. Geochemical comparison of oil-bearing fluid inclusions and produced oil from the Toro sandstone, Papua New Guinea. *Org. Geochem.* 26, 155–173.
- George, S.C., Lisk, M., Eadington, P.J., Quezada, R.A., Krieger, F.W., Greenwood, P.F., 1996. Comparison of palaeo oil charges with currently reservoired hydrocarbons using the geochemistry of oil-bearing fluid inclusions. Paper SPE 36980 presented at the 1996 SPE Asia Pacific Oil and Gas Conference in Adelaide, Australia 28–31 October. pp. 159–171.
- George, S.C., Lisk, M., Summons, R.E., Quezada, R.A., 1998. Constraining the oil charge history of the South Pepper oilfield from the analysis of oil-bearing fluid inclusions. *Org. Geochem.* 29, 631–648.
- Goldstein, R.H., 2001. Fluid inclusions in sedimentary and diagenetic systems. *Lithos* 55, 159–192 (this volume).
- Guilhaumou, N., Szydłowski, N., Pradier, B., 1990. Characterization of hydrocarbon fluid inclusions by infra-red and fluorescence microspectrometry. *Min. Mag.* 54, 311–324.
- Hagemann, H.W., Hollerbach, A., 1986. The fluorescence behaviour of crude oils with respect to their thermal maturation and degradation. *Org. Geochem.* 10, 473–480.
- Hanor, J.S., 1980. Dissolved methane in sedimentary brines: potential effect on the PVT properties of fluid inclusions. *Econ. Geol.* 75, 603–609.
- Horstad, I., Larter, S.R., Dypvik, H., Aagaard, P., Bjørnvik, A.M., Johansen, P.E., Eriksen, S., 1990. Degradation and maturity controls on oil field petroleum column heterogeneity in the Gullfaks field, Norwegian North Sea. *Org. Geochem.* 16, 497–510.
- Jensenius, J., Burruss, R.C., 1990. Hydrocarbon–water interactions during brine migration: evidence from hydrocarbon inclusions in calcite cements from Danish North Sea oil fields. *Geochim. Cosmochim. Acta* 54, 705–713.
- Karlsen, D.A., Nedkvitne, T., Larter, S.R., Bjørlykke, K., 1993. Hydrocarbon composition of authigenic inclusions: application to elucidation of petroleum reservoir filling history. *Geochim. Cosmochim. Acta* 57, 3641–3659.
- Katz, D.L., Firoozabadi, A., 1978. Predicting phase behavior of condensate/crude–oil systems using methane interaction coefficients. *Trans. AIME* 265, 1649–1655.
- Kesler, M.G., Lee, B.I., 1976. Improve prediction of enthalpy of fractions. *Hydrocarbon Process.* 55, 153–158.
- Khavari Khorasani, G., 1987. Novel development in fluorescence microscopy of complex organic mixtures: Application in petroleum geochemistry. *Org. Geochem.* 11, 157–168.
- Kihle, J., 1995. Adaptation of fluorescence excitation-emission micro-spectroscopy for characterization of single hydrocarbon fluid inclusions. *Org. Geochem.* 23, 1029–1042.
- Kihle, J., Andresen, B., Munz, I.A., 1995. Quantitative C_1 – C_{30+} extraction of hydrocarbons trapped as fluid inclusions; improved possibilities for isotope determinations and PVT modelling. In: Grimalt, J.O., Dorronsoro, C. (Eds.), *Organic Geochemistry: Developments and Applications to Energy, Climate, Environment and Human History*. pp. 736–738.
- Larter, S.R., Aplin, A.C., 1995. Reservoir geochemistry: methods, applications and opportunities. In: Cubitt, J.M., England, W.A. (Eds.), *The Geochemistry of Reservoirs* 86 Geol. Soc. London Spec. Publ., pp. 5–32.
- Leythaeuser, D., Rückheim, J., 1989. Heterogeneity of oil composition within a reservoir as a reflection of an accumulation history. *Geochim. Cosmochim. Acta* 53, 2119–2123.
- Lisk, M., George, S.C., Summons, R.E., Quezada, R.A., O'Brien, G.W., 1996. Mapping hydrocarbon charge histories: detailed characterisation of the South Pepper oil field, Carnarvon Basin. *APPEA* 36, 445–464.
- Mackenzie, A.S., 1984. Applications of biological markers in petroleum geochemistry. *Advances in Petroleum Geochemistry* 1 Academic Press, London, pp. 115–214.
- Mango, F., 1997. The light hydrocarbons in petroleum: a critical review. *Org. Geochem.* 26, 417–440.
- McLimans, R.K., 1987. The application of fluid inclusion to migration of oil and diagenesis in petroleum reservoirs. *Appl. Geochem.* 2, 585–603.
- Munz, I.A., Iden, K., Johansen, H., Vagle, K., 1998. The fluid regime during fracturing of the Embla field, Central Trough, North Sea. *Mar. Pet. Geol.* 15, 751–768.
- Munz, I.A., Johansen, H., Holm, K., Lacharpagne, J.-C., 1999a. The petroleum characteristics of the Frøy field and the Rind discovery, Norwegian North Sea. *Mar. Pet. Geol.* 16, 633–651.
- Munz, I.A., Johansen, H., Johansen, I., 1999b. Characterisation of composition and PVT properties of petroleum inclusions: Implications of reservoir filling and compartmentalisation. Paper SPE 56519 presented at the 1999 SPE Annual Technical Conference and Exhibition in Houston, 3–6 October 1999.
- Musgrave, J.A., Carey, R.G., Janecy, D.R., Tait, C.D., 1994. Adaption of synchronously scanned luminescence spectroscopy to organic-rich fluid inclusion microanalysis. *Rev. Sci. Instrum.* 65, 1877–1882.
- Narr, W., Burruss, R.C., 1984. Origin of reservoir fractures in Little Knife Field, North Dakota. *AAPG Bull.* 68, 1087–1100.
- Nedkvitne, T., Karlsen, D.A., Bjørlykke, K., Larter, S., 1993. Relationship between reservoir diagenetic evolution and petroleum emplacement in the Ula field, North Sea. *Mar. Pet. Geol.* 10, 255–270.

- Odden, W., 1999. A study of natural and artificially generated light hydrocarbons (C_4 – C_{13}) in source rocks and petroleum fluids from offshore Mid-Norway and the southernmost Norwegian and Danish sectors. *Mar. Pet. Geol.* 16, 747–770.
- Odden, W., Patience, R.L., Van Graas, G.W., 1998. Application of light hydrocarbons (C_4 – C_{13}) to oil/source rock correlations: a study of the light hydrocarbon compositions of source rocks and test fluids from offshore Mid-Norway. *Org. Geochem.* 28, 823–847.
- Osjord, E.H., Rønningsen, H.P., Tau, L., 1985. Distribution of weight, density and molecular weight in crude oil derived from computerized capillary GC analysis. *J. High Resolut. Chromatogr. Chromatogr. Commun.* 8, 683–690.
- Oxtoby, N., Mitchell, A.W., Gluyas, J.G., 1995. The filling and emptying of the Ula oilfield: fluid inclusion constraints. In: Cubitt, J.M., England, W.A. (Eds.), *The Geochemistry of Reservoirs 86 Geol. Soc. London Spec. Publ.*, pp. 141–157.
- Pedersen, K.S., Fredenslund, A., Thomassen, P., 1989. *Properties of Oils and Natural Gases*. Gulf Publishing.
- Péneloux, A., Rauzy, E., Fréze, R., 1982. A consistent correction for Redlich–Kwong–Soave volumes. *Fluid Phase Equilib.* 8, 7–23.
- Peng, D.-Y., Robinson, D.B., 1976. A new two-constant equation of state. *Ind. Eng. Chem. Fundam.* 15, 59–64.
- Pironon, J., Barres, O., 1990. Semi-quantitative FT-IR microanalysis limits: evidence from synthetic hydrocarbon fluid inclusions in sylvite. *Geochim. Cosmochim. Acta* 54, 509–518.
- Pironon, J., Canals, M., Dubessy, J., Walgenwitz, F., Laplace-Builhe, C., 1998. Volumetric reconstruction of individual oil inclusions by confocal scanning laser microscopy. *Eur. J. Mineral.* 10, 1143–1150.
- Pironon, J., Sawatzki, J., Dubessy, J., 1990. Chemical basis of fluorescence alteration of crude oils and kerogens: Part I. Microfluorimetry of an oil and its isolated fractions; relationships with chemical structure. *Org. Geochem.* 16, 451–460.
- Pradier, B., Largeau, C., Derenne, S., Martinez, L., Bertrand, P., Pouet, Y., 1990. Chemical basis of fluorescence alteration of crude oils and kerogens – I. Microfluorimetry of an oil and its isolated fractions; relationships with chemical structure. *Org. Geochem.* 16, 451–460.
- Riazi, M.R., Daubert, T.E., 1987. Characterization parameters for petroleum fractions. *Ind. Eng. Chem. Res.* 26, 755–759.
- Robinson, D.B., Peng, D.-Y., 1978. The characterization of the heptanes and heavier fractions for the GPA Peng–Robinson Programs. *Gas Processors Assoc., Res. Report RR-28*.
- Roedder, E., 1984. Fluid inclusions. *Mineral. Soc. Am., Rev. Mineral.* 12, 646 pp.
- Roedder, E., Bodnar, R.J., 1980. Geologic pressure determination from fluid inclusion studies. *Annu. Rev. Earth Planet. Sci.* 8, 263–301.
- Shepherd, T.J., Rankin, A.H., Alderton, D.H.M., 1985. *A Practical Guide to Fluid Inclusion Studies*. Blackie, Chapman & Hall, 239 pp.
- Soave, G., 1972. Equilibrium constants from a modified Redlich–Kwong equation of state. *Chem. Eng. Sci.* 27, 1197–1203.
- Stasiuk, L.D., Snowdon, L.R., 1997. Fluorescence micro-spectrometry of synthetic and natural hydrocarbon fluid inclusions: crude oil chemistry, density and application to petroleum migration. *Org. Geochem.* 12, 229–241.
- Stoddart, D.P., Hall, P.B., Larter, S.R., Brasher, J., Li, M., Bjørøy, M., 1995. The reservoir geochemistry of the Eldfisk field, Norwegian North Sea. In: Cubitt, J.M., England, W.A. (Eds.), *The Geochemistry of Reservoirs 86 Geol. Soc. London Spec. Publ.*, pp. 257–279.
- Ten Haven, H.L., 1996. Applications and limitations of Mango's light hydrocarbon parameters in petroleum correlation studies. *Org. Geochem.* 24, 957–976.
- Van den Kerkhof, A.M., Hein, U.F., 2001. Fluid inclusion petrography. *Lithos* 55, 27–47 (this volume).
- Whitson, C.H., 1983. Characterizing hydrocarbon plus fractions. *SPEJ* 23, 683–694.
- Wopenka, B., Pasteris, J.D., Freeman, J.J., 1990. Analysis of individual fluid inclusions by Fourier transform infrared and Raman microspectroscopy. *Geochim. Cosmochim. Acta* 54, 519–533.