ELSEVIER

Journal of Chromatography A, 824 (1998) 109–117

JOURNAL OF CHROMATOGRAPHY A

Separation of noble gas mixtures from petroleum and their isotopic analysis by mass spectrometry

Daniele L. Pinti*, Bernard Marty[1]

Laboratoire MAGIE, Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris Cedex 05, France

Received 25 March 1998; received in revised form 6 July 1998; accepted 6 July 1998

Abstract

Considerable information on oil exploration can be gained from the isotopic measurement of noble gases dissolved in petroleum. However, this analysis is complicated by (i) incomplete degassing, due to the high solubility of noble gas in petroleum, and (ii) pollution of the analytical devices by organic compounds. Here, a specific facility for the separation of noble gases from petroleum is described. The separation is based on the release of the gases dissolved in petroleum into the headspace of an evacuated container (flashing). Purification of noble gases from reactive gases is performed by using CuO furnaces and Ti–Zr alloy getters. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Petroleum; Extraction methods; Oils; Cryogenic separation; Instrumentation; Mass spectrometry; Geochemistry; Noble gases; Gases

1. Introduction

Noble gases, inert, low in abundance and highly mobile elements, are ideal tracers of fluid movement throughout the continental crust [1–3]. Since the earlier work of Zartman et al. [1] noble gases have been used to trace the origin and the migration of natural gas accumulations in sedimentary basins [2–5]. Particularly useful are the atmosphere-derived noble gases (ANGs). ANGs are transported by groundwater which has equilibrated with the atmosphere [6,7]. Since noble gases are more soluble in oil [8] than in water [9], mixing between petroleum and groundwater is expected to result in a preferential partitioning of ANGs in petroleum. Therefore, the ANG amount in petroleum can provide an indication of the scale of groundwater flow in oil fields [2]. Finally, mantle-derived noble gas isotopes, such as primordial ^{3}He, can provide information on deep sources of natural gas deposits [3,5].

To date, noble gas studies of hydrocarbons have been restricted to natural gas reservoirs. Only recently Pinti and Marty [10] and Ballentine et al. [11] have carried out the first complete noble gas studies of a petroleum phase. There are several reasons for such a limited number of studies. On one hand there

*Corresponding author. Present address: c/o Prof. Philippe Sarda, Groupe de Geochimie des Gaz Rares d'Orsay, Université Paris 11, Batiment 504 3^{e} etage, 91405 Orsay Cedex, France. Fax: +33-1-6915-4917.

[1] Present address: Centre des Recherches Pétrographiques et Géochimiques, BP 20, 54501 Vandoeuvre Cedex and École Nationale Supérieure de Géologie, 1 Rue du Doyen Roubault, 54501 Vandoeuvre Cedex, France.

0021-9673/98/$ – see front matter © 1998 Elsevier Science B.V. All rights reserved.
PII: S0021-9673(98)00566-4

is the limited access to oil samples. On the other hand, there are analytical difficulties resulting from the incomplete separation from petroleum of the dissolved noble gases, and the pollution with hydrocarbons assemblages of ultra-clean instruments such as the noble-gas mass spectrometry (NGMS systems).

Incomplete degassing of noble gases occurs because their high solubility in oil [8]. Thus, a complete separation of noble gases from petroleum requires the use of specific devices. The purification of noble gases from petroleum is another critical step in the process. If incomplete purification occurs, gaseous hydrocarbons can deposit on the walls of the mass spectrometer flight tube, promoting the adsorption of heavy noble gases, particularly xenon, and increase background levels. Furthermore, several hydrocarbon masses overlap those of the noble gas isotopes introducing high uncertainties in the isotopic analysis (Fig. 1).

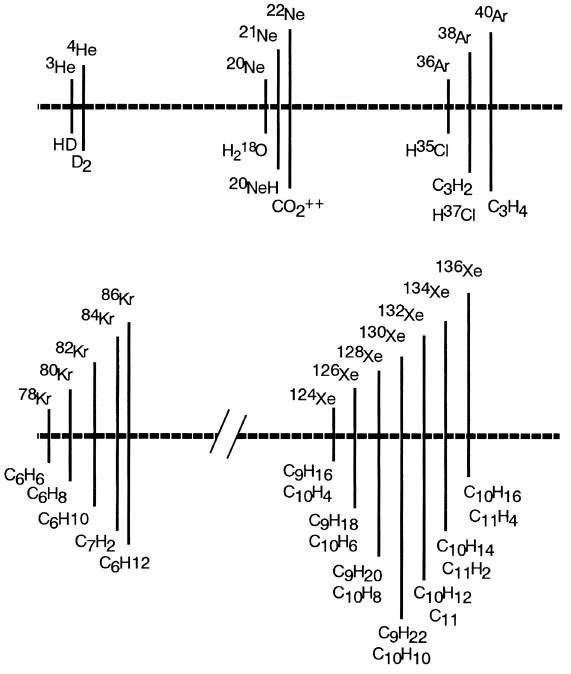

Fig. 1. Spectra of hydrocarbon and chlorine isotopes (the latter contained in the brine water associated with petroleum) which can interfere with the measurement of the noble gas isotopes.

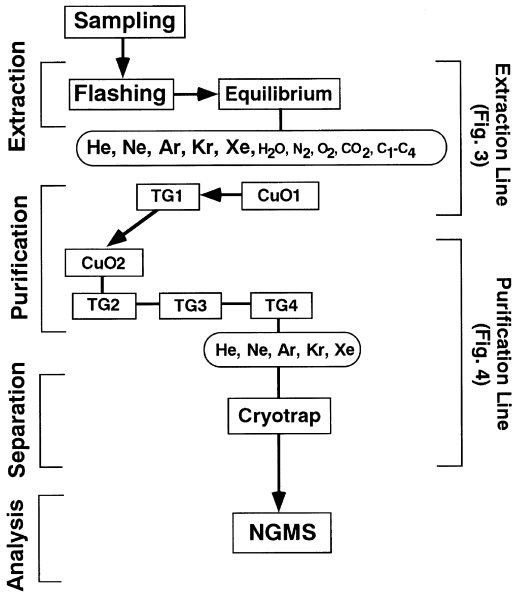

Fig. 2. Flow chart of the extraction, purification and analysis procedure of noble gases in petroleum. Legend: CuO = copper oxide getter; TG = Ti–Zr alloy getter; NGMS = noble gas mass spectrometry system.

In the present paper, we describe the procedure used at the Université 'Pierre et Marie Curie' (UPMC), for the separation and purification of noble gases from petroleum and their elemental and isotopic analysis by NGMS. This procedure includes four basic steps (Fig. 2): (i) gas extraction; (ii) gas purification; (iii) cryogenic separation of noble gas species; (iv) isotopic measurements by mass spectrometry.

A specific extraction facility has been developed in order to extract noble gases from petroleum samples collected in soft-annealed copper tubes (0.95 cm diameter; 13 cm^3 in volume) cold-sealed with pinch-off clamps (Fig. 3). The facility is connected directly to a preexisting stainless-steel purification line (Fig. 4) used for routine analysis of noble gases in fluid and rock samples [12]. The described instrumental facility was used for a complete study of noble gases in petroleum from the Middle Jurassic and Triassic reservoirs of the Paris Basin, Northern France [10].

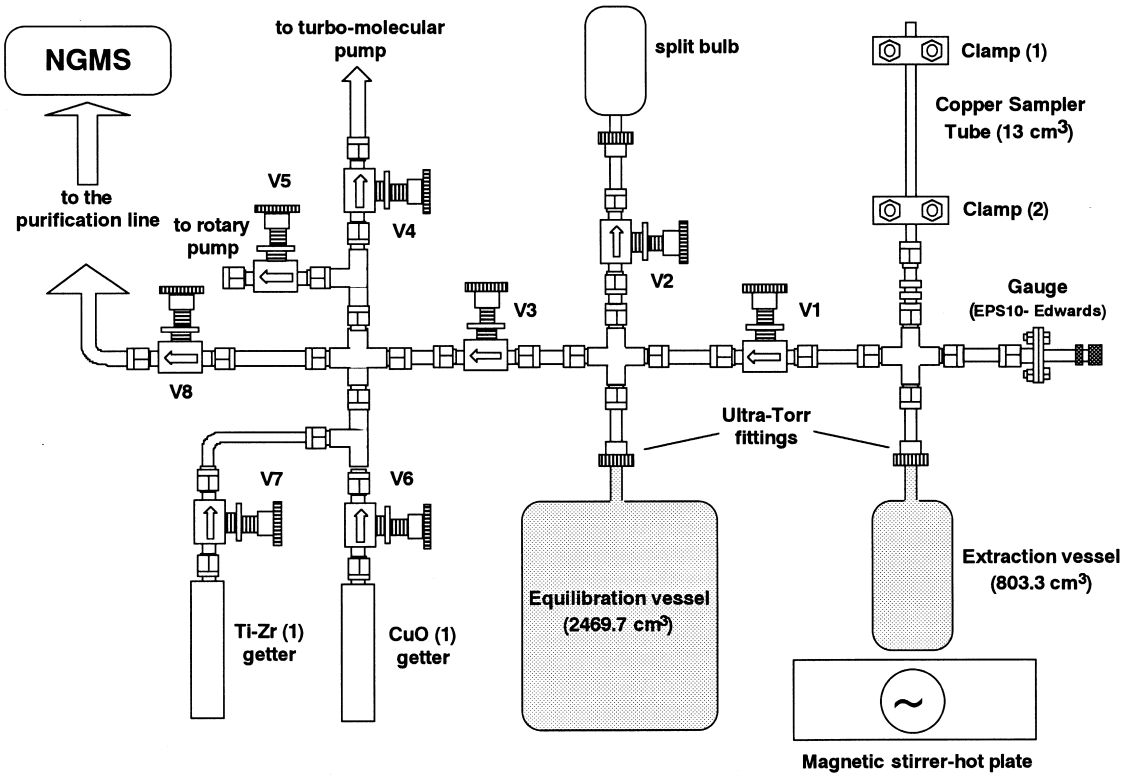

Fig. 3. Schematic of the extraction line.

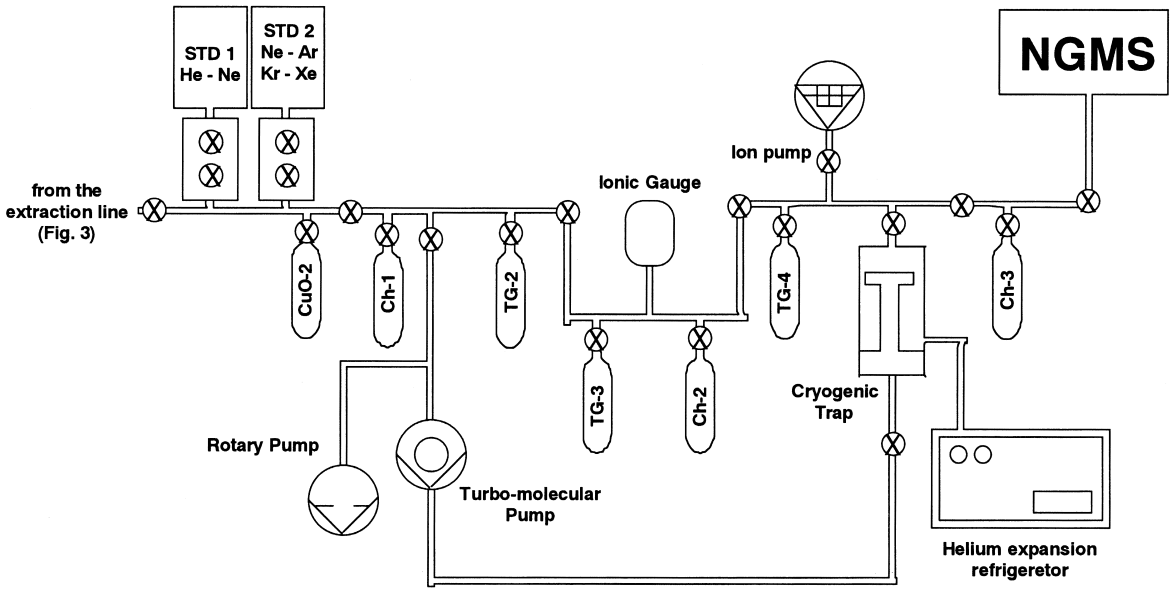

Fig. 4. Schematic of the purification line. Legend: STD = standard air; Ch = charcoal trap; CuO = copper oxide; TG = Ti–Zr alloy getter.

2. Separation of noble gas mixtures from petroleum

2.1. Mathematical background

The extraction of noble gases from petroleum is based on the degassing of a fluid of volume V_l into a closed volume V_g, previously evacuated. At equilibrium the fraction of extracted gas (E) is:

$$E = [1 + (n_l/n_g)]^{-1} \quad (1)$$

where n_l and n_g are the moles of gas in the liquid and in the gas phase, respectively. At equilibrium, n_l and n_g are equal to:

$$n_l = [(PV_l)/K] \quad (2)$$

$$n_g = [(PV_g)/(RT)] \quad (3)$$

where P is the gas pressure (atm), R the gas constant (0.082056 l atm K^{-1} mol^{-1}), T the absolute temperature (K), and K (l atm mol^{-1}) the gas solubility, constant (at 1 atm = 101 325 Pa). The latter is an approximation of the Henry's constant of solubility and is appropriate for a heterogeneous liquid, such as petroleum [8]. Substituting in Eq. (1) Eqs. (2) and (3), we obtain:

$$E = \{[(V_l/V_g) \times (RT/K)] + 1\}^{-1} \quad (4)$$

Thus the extraction of gas depends critically on the ratio V_g/V_l, with an increase promoting degassing. Eq. (5) is valid when only a single liquid phase occurs (water or oil). However, oil samples are generally a mixture of saline waters (brine) and liquid hydrocarbons. In this more complicated system, Eq. (2) becomes:

$$n_l = [(V_o/K_o) + (V_w/K_w)] \quad (5)$$

where suffix 'o' and 'w' is for the oil and water phase. Consequently, Eq. (4) becomes:

$$E = \left(\left\{ \frac{RT[(V_o/K_o) + (V_w/K_w)]}{V_g} \right\} + 1 \right)^{-1} \quad (6)$$

The fraction of extracted gas has been calculated using Eq. (4) for all the noble gases, for different ratios V_g/V_l and at room temperature (Fig. 5). Two limiting cases are considered. The first case is pure oil solvent. At 25°C, the solubility of He, Ne, Ar, Kr and Xe in a light oil (oil density = 0.85 g/cm^3) is 3, 2, 7, 12 and 24 times higher than in pure water [8]. In this case, the extraction of gas is not facilitated. The second case is the extraction of gas from brine water. The occurrence of salt ions in the solution decreases the solubility of noble gases, promoting

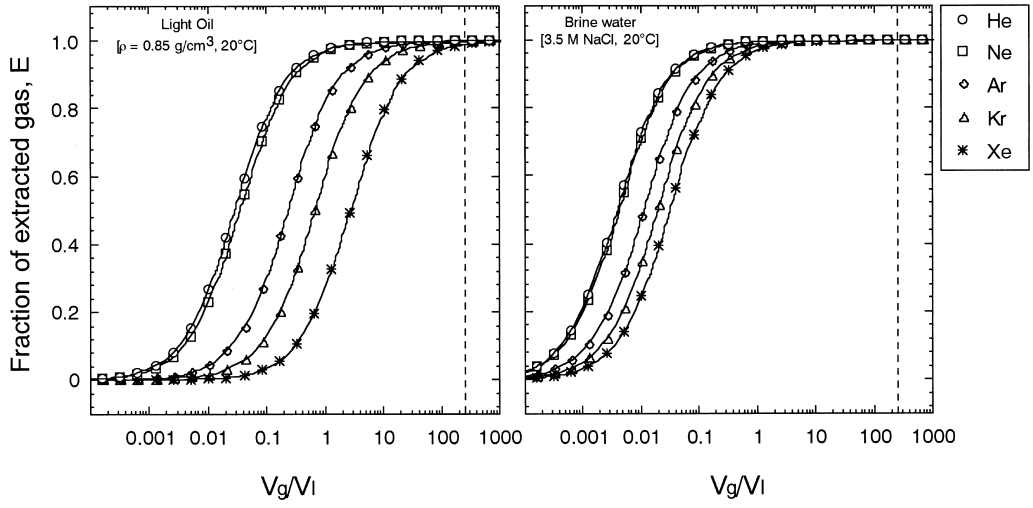

Fig. 5. Theoretical curves of extraction of noble gases calculated by using Eq. (4). Curves are for a light oil (oil density = 0.85 g/cm^3) and a brine water [total dissolved salinity (TDS) = 3.5 M NaCl], at room temperature. The dashed lines indicate the ratio V_g/V_l in our extraction facility.

degassing [9]. From the theoretical extraction curves (Fig. 5), it is observed that the volume ratio V_g/V_l needed for a 99.99% extraction of He and Xe (the least and the most soluble noble gas, respectively) from an oil sample are of ~10 and 1000, respectively. For a brine water, these ratios decrease to ~1 and ~10.

2.2. Description of the extraction facility

A detailed schematic of the noble gas extraction facility built at UPMC is reported in Fig. 3. The extraction line (Fig. 3) is made of stainless steel Cajon VCR components connected with copper O-rings. The total volume of the line, excluding the collection and expansion vessel, the CuO and the Ti–Zr getter, is 26.21 cm^3. The different sections of the line are isolated by high-vacuum Nupro SS-4BG-V51 stainless steel valves. The collection vessel ($V_1 = 803.3$ cm^3) and the expansion flask ($V_2 = 2469.7$ cm^3) are made of Corning 1723 glass [13]. The choice of this expensive Al_2O_3 and MgO-rich glass was dictated by its very low permeability to noble gases, particularly to He (permeation rate $K_{He} = 4.5 \cdot 10^{-19}$ mol s^{-1} cm^{-2} mm^{-1} $Torr^{-1}$) compared to the Pyrex 7740 ($K_{He} = 1.5 \cdot 10^{-11}$ mol s^{-1} cm^{-2} mm^{-1} $Torr^{-1}$) (1 Torr = 133.322 Pa) [14]. These characteristics enable us to obtain the required blanks during the degassing of the petroleum samples (Table 1). The vessels are removed from the line and cleaned separately after each extraction from the residual petroleum. The connection between the Corning 1723 vessels and the metallic line is made through two Cajon Ultra-Torr Fittings, which provide a vacuum-tight seal with quick, finger-tight assembly between glass and metal. A magnetic stirrer/hot plate is located under the collection vessel to improve the extraction efficiency. A total pressure gauge Edwards EPS-10 (range 1–1700±1% mbar) is installed close to the extraction vessel to measure the initial pressure of the gas mixture. A CuO furnace and a Ti–Zr alloy getter complete the line (Fig. 3). The line is baked at 150°C after each extraction, and pumped by a rotary pump and a turbo-molecular pump, to a residual pressure of $<10^{-7}$ bar.

2.3. Extraction procedure

The 13-cm^3 copper tube containing the oil is vertically connected to the extraction line over the collection vessel (Fig. 3). First, the lower pinch-off clamp is removed, then the tube opened and the oil sample drained into the collection vessel. The sample is magnetically stirred, but not heated to avoid the creation of a high-molecular mass hydrocarbon gas phase. The gas contained in the copper tube + vessel volume is then equilibrated with the expansion flask volume. This equilibration also enable us: (i) to dilute the gas mixtures in case of high gas pressure; and (ii) to prevent oil particles contaminating the pre-purification traps CuO1 and TG1 (Fig. 3). Indeed, suspended particles of oil are easily transported by the gas phase into the expansion vessel, as observed in very high gas pressure samples (Triassic oils T9 and T10, Paris Basin; [10]). The ratio of the total volume of expansion ($V_1 + V_2 = V_g = 803.3 + 2469.7$ cm^3) to the volume of liquid ($V_l = 13$ cm^3) is 251 in our extraction line. The flashing due to the high gas–liquid ratio produces the extraction of most of the gas contained in oil (Fig. 5). The theoretical extraction efficiency in our line for Xe (the most soluble noble gas in petroleum) is 98.97%, for a pure oil sample. Repeated measurements of the residual

Table 1
Comparison within procedural blanks of noble gas measurement in petroleum and natural gas samples

Gas	Amount (mol)			
	This study	Ref. [2]	Ref. [4]	Ref. [5]
^4He	$0.9–4.4 \cdot 10^{-14}$	$1.3–3.1 \cdot 10^{-14}$	$1.0–1.2 \cdot 10^{-12}$	$1.3–3.0 \cdot 10^{-12}$
^{20}Ne	$0.6–6.8 \cdot 10^{-16}$	$1.3–3.1 \cdot 10^{-16}$	$1.4–1.7 \cdot 10^{-14}$	$0.9–9 \cdot 10^{-16}$
^{40}Ar	$0.3–1.5 \cdot 10^{-14}$	$0.9–1.8 \cdot 10^{-12}$	$0.9–7.4 \cdot 10^{-12}$	$<3.0 \cdot 10^{-14}$
^{84}Kr	$0.2–1.1 \cdot 10^{-18}$	–	–	$2.2–3.1 \cdot 10^{-18}$
^{132}Xe	$0.6–7.2 \cdot 10^{-20}$	–	-	$2.2–4.0 \cdot 10^{-19}$

Xe in the line for two petroleum samples from the Paris Basin confirmed that ~98% of the gases were extracted with this facility [10]. The time of equilibration needed to reach such an extraction is 30 min.

3. Purification procedure

The purification of the gas mixture is carried out in two distinct cycles: (1) a pre-purification cycle in the extraction line (Fig. 3), and (2) a complete purification cycle in the multipurpose line connected with the NGMS system (Fig. 4). A gas aliquot of 13.1 cm^3 is isolated in the last volume of the extraction line, between valve V3, V4 and V8 (Fig. 3). The aliquot is exposed to a CuO furnace, firstly heated from 450°C to 800°C over 15 min, then kept at 800°C for 20 min and finally cooled slowly (15 min) to room temperature. The heated CuO supplies an oxygen-rich atmosphere which oxidizes the alkanes (C_1–C_4) to CO_2 and H_2O. The resulting gas mixture is then exposed to a Ti–Zr alloy getter, heated at 800°C for 20 min and then cooled at room temperature for 20 min. During the high-temperature stage H_2O, O_2, N_2, CO_2 are removed through reaction with the Ti. The partial pressure of H_2 is reduced during the low-temperature stage. The pre-purified aliquot is then introduced into the purification line (Fig. 4). The line is equipped with three further Ti–Zr alloy getters, one CuO furnace, and a cryogenic trap for the separation of the single noble gas species. Three charcoal traps complete the line. During the second cycle of purification, the gas aliquot is exposed again over the CuO furnace (20 min at 600°C and 20 min at room temperature) and successively purified on the three Ti–Zr alloy getters (20 min at 800°C and 20 min at room temperature).

The remaining noble gases are then adsorbed onto a Solartron Cryogenics cryogenic trap (Fig. 4). The cold head contains a sintered stainless-steel grid with pores having a diameter of 0.25 μm. The grid is cooled to a minimum of 9 K by using an helium expansion refrigerator. The temperature of desorption of the noble gases is monitored by using a Pt-Pt/Rh thermocouple, with a precision of ±0.3°C. Typical temperatures of desorption of the noble gases are: He (15.0±0.2 K), Ne (39.2±0.2 K), Ar (91.4±0.3 K), Kr (118.3±3.0 K) and Xe (149.0±6.6 K). Desorption curves of He, Ne, Ar, Kr and Xe are reported in Fig. 6. The adsorption energy (ε) of each noble gas for the stainless steel cold head has been determined from the least square fitting of the data shown in Fig. 6 as $|\varepsilon_{He}| = 5.1 \cdot 10^{-21}$ J, $|\varepsilon_{Ne}| = 1.3 \cdot 10^{-20}$ J, $|\varepsilon_{Ar}| = 3.5 \times 10^{-20}$ J, $|\varepsilon_{Kr}| = 4.5 \cdot 10^{-20}$ J, $|\varepsilon_{Xe}| = 5.8 \cdot 10^{-20}$ J. These values are compatible with those reported in literature for stainless steel as $|\varepsilon_{Ar}| = 4.0 \cdot 10^{-20}$ J, $|\varepsilon_{Kr}| = 4.8 \cdot 10^{-20}$ J, $|\varepsilon_{Xe}| = 6.35 \cdot 10^{-20}$ J [15]. Because of the release of a substantial amount of Xe (up to 20%) together with Kr (Fig. 6), we decided to release both gases at 180 K and send together into the NGMS system for isotopic analysis.

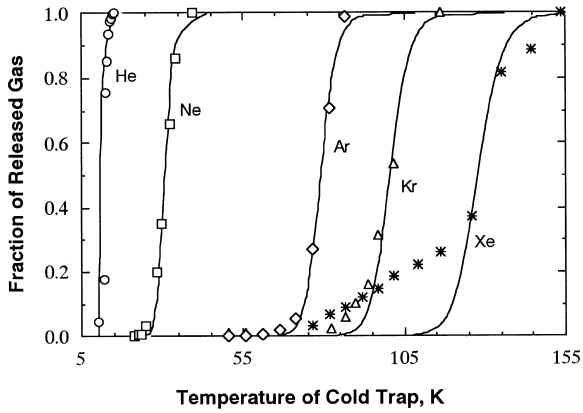

Fig. 6. Desorption curves of He, Ne Ar, Kr and Xe for the stainless steel cold head. The solid lines were obtained by a least square fitting of a Langmuir adsorptive equation [15]. Symbols as in Fig. 5.

4. Mass spectrometry

A sector-type mass spectrometer (VG5400, Fisons) has been used to analyze the elemental and isotopic abundance of noble gases in petroleum. The VG5400 at UPMC is equipped with an electron impact ion source (Nier Type) and three ion collectors: two Faraday cups and a Daly collector. The mass resolution ($M/\Delta M$) is adjusted to about 750 for the Daly collector and 250 for the Faraday collectors. The source conditions are set differently for the

analysis of helium isotopes ^{3}He and ^{4}He and for the others noble gas isotopes ($^{20-22}$Ne, $^{36-40}$Ar, $^{78-86}$Kr and $^{124-136}$Xe). For He analysis, the trap current is set at 800 μA and the electron energy at 100 eV. For the Ne-Xe analysis, the trap current was set at 400 μA and the electron energy at 58 eV. Helium, neon and argon isotope analyses were performed using the Daly collector for ^{3}He, $^{21-22}$Ne and $^{36-38}$Ar ion beams and using the Faraday collector for the more abundant isotopes ^{4}He, ^{20}Ne and ^{40}Ar. Kr and Xe isotopes are analyzed exclusively on the Daly collector. During the neon isotope analysis, appropriate mass peaks were monitored to correct for interference due to doubly charged ions on ^{20}Ne, on ^{22}Ne, $^{20}NeH^{+}$ on ^{21}Ne, and interfering contaminant H_2 $^{18}O+$ on ^{20}Ne. During the analysis of petroleum samples [10], the double charge correction for ^{20}Ne ($^{40}Ar^{2+}$) was 0.3–4% of the measured value, that for ^{22}Ne of 0.1–0.5%. No interference at masses 36 and 38 from HCl has been observed.

Our main concern was to test the efficiency of the hydrocarbon and chlorine purification. Typical procedural blanks during petroleum analysis are reported in Table 1. The measured values are in the range of the procedural blanks observed during noble gas analysis in CH_4-rich samples or lower, for Kr and Xe (Table 1). The measured levels of blank were always 100–1000× lower than the measured noble gas amounts in the oils and thus negligible [10]. No anomalous increase on the blank amount of ^{36}Ar or ^{132}Xe (index of chlorine and hydrocarbon contamination, respectively) have been observed (Fig. 7).

The calibration of the system was made with two standards. The first standard (STD1) contains 24.2% of He and 75.8% of Ne, and is used for the calibration of the analyzer for helium isotope analysis (Fig. 4). The second (STD2) is a purified sample of air containing He (0.06%), Ne (0.19%), Ar (99.7%), Kr (0.013%) and Xe (0.0009%), to calibrate the analyzer for Ne through Xe. Noble gas sensitivities (over a period of 3 months) were $3.8\cdot10^{-5}\pm0.5\%$ A/Torr (^{4}He), $5.9\cdot10^{-5}\pm2.2\%$ A/Torr (^{20}Ne), $4.9\cdot10^{-4}\pm2.3\%$ A/Torr (^{40}Ar), $3.6\cdot10^{-5}\pm14.2\%$ A/Torr (^{84}Kr), $6.4\cdot10^{-4}\pm3.0\%$ A/Torr (^{132}Xe). The sensitivities are in the same range of those recorded during routine analysis prior and after the analysis of petroleum. For helium isotope measurements, the system calibrated with standard

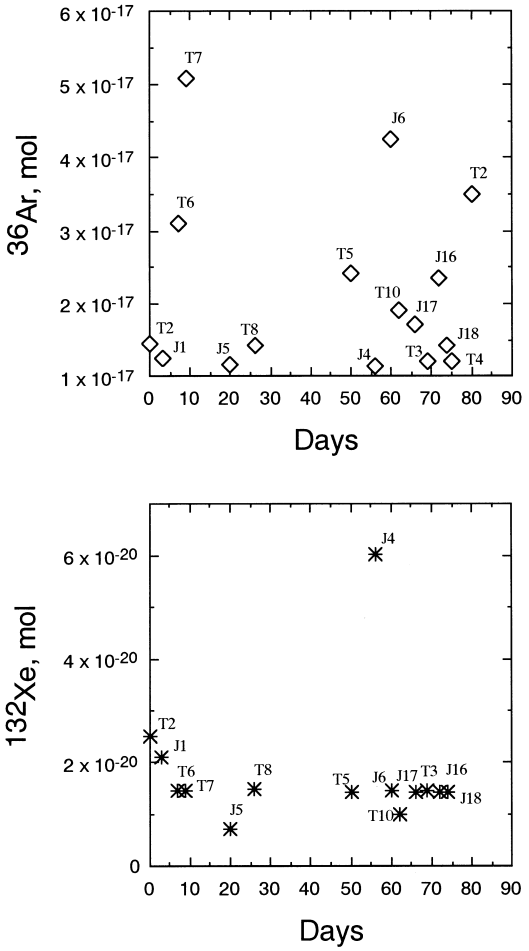

Fig. 7. Temporal variations of the blank amount of ^{36}Ar and ^{132}Xe, measured during the analysis of petroleum samples from the Paris Basin, France [10].

STD1 gave $^{3}He/^{4}He$ ion beam ratios of $1.2\cdot10^{-6}$, with typical reproducibility of 0.99% (Fig. 8) for $1.2\cdot10^{-11}$ mol ^{4}He, over a period of 1 month. For all the other noble gases, the system calibrated with standard STD2 gave typical reproducibility of 0.23% for $^{20}Ne/^{22}Ne$, of 0.21% for $^{38}Ar/^{36}Ar$ and 1.6% for $^{130}Xe/^{132}Xe$, over a 3-months period (Fig. 8).

5. Conclusions

A specific facility for the extraction of noble gas from petroleum has been developed at UPMC, to assure precise isotopic measurements of He, Ne, Ar,

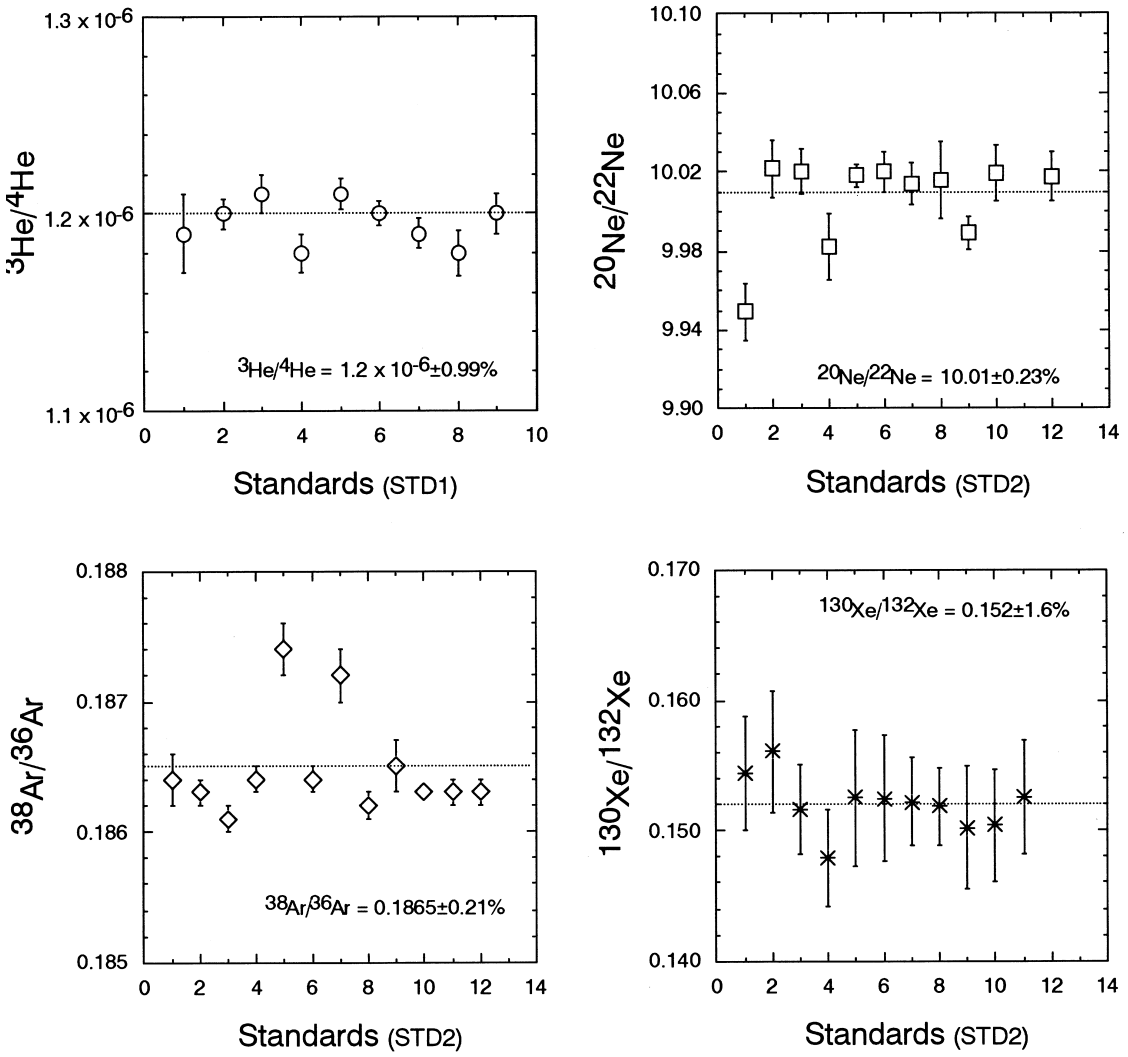

Fig. 8. Noble gas isotopic ratios measured in standard air, during the analysis of petroleum samples from the Paris Basin, France [10].

Kr and Xe by mass spectrometry. The extraction procedure is based on the flashing of the petroleum samples in a volume previously evacuated. The geometry of our facility allows the extraction of more than 98% of the noble gases dissolved in the hydrocarbon assemblage in a short span of time (30 min). Several stages of purification of the noble gas mixture from reactive gases, hydrocarbons and organic compounds are performed by using copper oxide traps and Ti–Zr alloy getters. Finally, a cryogenic trap is used to separate the single noble gas species for the isotopic measurements. During three months work for the analysis of 17 crude oils from the Paris Basin, France [10], no interfering hydrocarbon masses were detected, nor have we observed any anomalous increase of the blank level on the heavy noble gas masses, which would indicate pollution of the mass spectrometer flight tube by organic compounds.

Acknowledgements

We acknowledge the invaluable contribution of the

technical staff at UPMC (N. Vassard, M. Lenoble, C. Innocent, B. Giraud), without whose skills this work could not have been completed. We wish to thank A. Jambon for his encouragement and valuable suggestions during our stay at Laboratoire MAGIE. Reviewing by A.Y. Huc (IFP, Paris, France) has much improved this manuscript. The research of D.L.P. at UPMC was supported by a EU sectorial grant (contract No. ERBJOUFCT913001).

References

[1] R.E. Zartman, G.J. Wasserburg, J.H. Reynolds, J. Geophys. Res. 66 (1961) 277.
[2] C.J. Ballentine, R.K. O'Nions, E.R. Oxburgh, F. Horvarth, J. Deàk, Earth Planet. Sci. Lett. 105 (1991) 229.
[3] H. Hiyagon, B.M. Kennedy, Geochim. Cosmochim. Acta 56 (1992) 1569.
[4] T. Elliot, C.J. Ballentine, R.K. O'Nions, T. Ricchiuto, Chem. Geol. 106 (1993) 429.
[5] S. Xu, S. Nakai, H. Wakita, X. Wang, Geochim. Cosmochim. Acta 59 (1995) 4675.
[6] C.J. Ballentine, R.K. O'Nions, in: J. Parnell (Ed.), Geofluids: Origin, Migration and Evolution of Fluids in Sedimentray Basins, Special Publication No. 78, Geological Society, London, p. 347.
[7] A. Bosch, E. Mazor, Earth Planet. Sci. Lett. 87 (1988) 338.
[8] Y.K. Kharaka, D.J. Specht, Appl. Geochem. 3 (1988) 137.
[9] S.P. Smith, B.M. Kennedy, Geochim. Cosmochim. Acta 47 (1983) 503.
[10] D.L. Pinti, B. Marty, Geochim. Cosmochim. Acta 59 (1995) 3389.
[11] C.J. Ballentine, R.K. O'Nions, M.L. Coleman, Geochim. Cosmochim. Acta 60 (1996) 831.
[12] B. Marty, M. Lenoble, N. Vassard, Chem. Geol. 120 (1995) 183.
[13] P. Jean-Baptiste, C. Andrie, M. Lelu, Glass Technol. 30 (1989) 228.
[14] F.J. Norton, J. Am. Ceram. Soc. 36 (1956) 90.
[15] T. Maruoka, J. Matsuda, J. Mass. Spectrom. Soc. Jpn. 43 (1995) 1.