

**Comparative Ebulliometry: a Simple, Reliable
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Average Molecular Weight of Macromolecules.
Preliminary Studies on Heavy Crude Fractions**

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COMPARATIVE EBULLIOMETRY: A SIMPLE, RELIABLE TECHNIQUE FOR ACCURATE MEASUREMENT OF THE NUMBER AVERAGE MOLECULAR WEIGHT OF MACROMOLECULES

PRELIMINARY STUDIES
ON HEAVY CRUDE FRACTIONS

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ÉBULLIOMÉTRIE COMPARATIVE : TECHNIQUE SIMPLE
ET FIABLE POUR DÉTERMINER PRÉCISÉMENT
LA MASSE MOLAIRE MOYENNE EN NOMBRE
DES MACROMOLÉCULES

ÉTUDES PRÉLIMINAIRES SUR DES FRACTIONS LOURDES DE BRUTS

Cet article comprend deux parties. Dans la première, les auteurs présentent une comparaison entre les principales techniques de détermination de la masse molaire de macromolécules. Les résultats de l'étude bibliographique sont rassemblés dans plusieurs tableaux.

La seconde partie décrit un ébulliomètre comparatif conçu pour la mesure de la masse molaire moyenne en nombre (M_n) des fractions lourdes des bruts. Une illustration de l'efficacité de cet appareil est indiquée avec l'étude préliminaire de résidus de distillation atmosphérique et de résines. En particulier, la mesure de masses molaires pouvant atteindre 2000 g/mol est possible en moins de 4 heures avec une incertitude expérimentale de l'ordre de 2 %.

COMPARATIVE EBULLIOMETRY: A SIMPLE, RELIABLE
TECHNIQUE FOR ACCURATE MEASUREMENT
OF THE NUMBER AVERAGE MOLECULAR WEIGHT
OF MACROMOLECULES

PRELIMINARY STUDIES ON HEAVY CRUDE FRACTIONS

This article is divided into two parts. In the first part, the authors present a comparison of the major techniques for the measurement of the molecular weight of macromolecules. The bibliographic results are gathered in several tables. In the second part, a comparative ebulliometer for the measurement of the number average molecular weight (M_n) of heavy crude oil fractions is described. The high efficiency of the apparatus is demonstrated with a preliminary study of atmospheric distillation residues and resins. The measurement of molecular weights up to 2000 g/mol is possible in less than 4 hours with an uncertainty of about 2%.

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EBULLIOMETRÍA COMPARATIVA : TÉCNICA SENCILLA
Y FIABLE PARA DETERMINAR CON TODA PRECISIÓN
LA MASA MOLAR MEDIA EN NÚMERO DE LAS
MACROMOLÉCULAS

ESTUDIOS PRELIMINARES MEDIANTE FRACCIONES
PESADAS DE CRUDOS

Este artículo consta de dos partes. En la primera, los autores presentan una comparación entre las principales técnicas de determinación de la masa molar de macromoléculas. Los resultados del estudio bibliográfico figuran reunidos en varias tablas. En la segunda parte, se describe un ebuliómetro comparativo diseñado para la medición de la masa molar de promedio en número (M_n) de las fracciones pesadas de los crudos. Una ilustración de la eficacia de este aparato se indica con el estudio preliminar de residuos de destilación atmosférica y de resinas. Básicamente, existe la posibilidad de obtener la medición de las masas molares que pueden alcanzar 2 000 g/mol, en menos de 4 horas, con una incertidumbre experimental de, aproximadamente, un 2 %.

INTRODUCTION

The average molecular weights of a crude oil and of its fractions are fundamental data, which are required in the petroleum industry to develop descriptive and predictive compositional thermodynamic models. The equipment generally used in this industry to measure such values are the vapor pressure osmometers (VPO or industrial tonometers). These osmometers often cannot give results with an accuracy better than about 10% for average molecular weights above 1000 g/mol.

Various studies have been carried out using mass spectrometry, size exclusion chromatography (gel permeation), X-ray or neutron diffusion, VPO, etc., to obtain more accurate results. However, in every case, the analysis requires either time or money and significant analytical and technical expertise. Thus, these methods can be used only in an analytical center dedicated to research.

In this context, the ebulliometric measurement of molecular weight appears to be a good compromise in terms of cost, accuracy, time and simplicity. The possibility of measuring the molecular weight in a "routine way" gives ebulliometry an important advantage that will be shown below.

During this study on the measurement of the molecular weight of heavy crude oil fractions, we have encountered numerous data relative to various measurement techniques for the molecular weight of macromolecules. Although not always in line with our purpose, these data are still interesting for those who are looking for a short review of the major techniques of molecular weight measurement. Hence, the first part of this article consists of tables which bring together information on molecular weight measurement: techniques, authors, ranges of molecular weights, ranges of sample concentrations, types of molecular weights, experimental uncertainty, measurement times and types of macromolecules.

These tables are not exhaustive and are not completely filled in because some information is not given in the original articles. We hope, nevertheless, that they will be useful and that they will give an overview of this very delicate but fundamental experimental practice.

The second part of the paper is a presentation of the ebulliometric method for measuring molecular weight. After a short review of the basic principles, we describe our ebulliometer. Then, we show the preliminary results of a study on heavy crude fractions and the outlook for

the future. The reader can find more extensive information in the work of D. Vellut [87].

PART 1 – VARIOUS TECHNIQUES FOR MEASURING THE MOLECULAR WEIGHT OF MACROMOLECULES

The experimental uncertainty noted in the following tables is, in fact, of different types. It could be due either to the reproducibility, the repeatability or the accuracy of the measurement. In these cases, the molecular weight (MW) could be estimated by MW = result ± experimental uncertainty.

It could also be due to the deviation from other techniques, in which case the data are given in the following form: uncertainty/technique which means “the deviation of the result from this technique is...”.

At first we wanted to summarize the data for each technique in a single line, but the results are so different, even for the same technique, that this would lose any interest. In effect, except for the measurement time, the other average parameters would be the same for all the techniques. Therefore, the results found in the literature are simply listed without comment.

Notation [83]:

– Number average molecular weight M_n :

$$\overline{M_n} = \frac{\sum_i n_i M_i}{\sum_i n_i} = \frac{\sum w_i}{\sum w_i / M_i}$$

– Weight average molecular weight M_w :

$$\overline{M_w} = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i} = \frac{\sum w_i M_i}{\sum w_i}$$

THERMODYNAMIC COLLIGATIVE METHODS

Ref. no.	Techniques and authors	Range of molecular weight (g/mol)	Range of concentration	Type of molecular weight	Experimental uncertainty	Duration of experimentation	Type of macromolecules analysed (asphaltenes, crude fractions, polymers, etc.)
1. EBULLIOMETRY							
[1]	HILL F.N. <i>et al.</i> , 1950 (Differential Ebulliometry (D.Ebu.))	300-15 000	< 5%(w/wt)	M_n	> 2%	4 h	glycol polyethylene and vinyl acetate chloride copolymers
[2]	RAY N.H., 1952 (D.Ebu.)	< 35 000	> 5% (w/wt)	M_n	5-10%	4 h	polythenes
[3]	SMITH H., 1956 (D.Ebu.)	< 30 000	5-15% (w/wt)	M_n	5-10%	4 h	polythenes
[4]	DIMBAT M. <i>et al.</i> , 1957 (Comparative Ebulliometry (C.Ebu.))	< 20 000	0.1-0.5% (w/wt)	M_n	*	4 h	*
[5]	GRIFFIN <i>et al.</i> , 1958 (D.Ebu.)	2500-4000	*	M_n	*	*	asphaltenes
[6]	LEHRLE R.S. <i>et al.</i> , 1958 (D.Ebu.)	< 40 000	0.1-3% (w/wt)	M_n	< 5%	*	polycaprolactams
[7]	KYRITSOS J., 1966 (oscillating ebulliometer)	< 20 000	1-5% (w/wt)	M_n	5%	> 4 h	polystyrenes
[8]	TSUCHIDA E. <i>et al.</i> , 1970	300-10 000	5-50 mg/ml	M_n	< 3%	*	poly(ethylene glycols), polystyrene
[9]	GLOVER <i>et al.</i> , 1972 (D.Ebu.)	< 170 000	*	M_n	1-6%	*	polyglycol, polyethylene, polystyrene, organosilicon
[10]	PARRINI P. <i>et al.</i> , 1974 (D.Ebu.)	< 100 000	> 20% (w/wt)	M_n	< 6.5%	4 h	polypropylenes
[11]	VELLUT D. <i>et al.</i> , 1996 (C.Ebu.)	150-1000	1-5% (w/wt)	M_n	< 2%	4 h	petroleum cuts: maltenes atmospheric residues, resins, etc.
2. CRYOMETRY							
[12]	SAAL R.M. <i>et al.</i> , 1946	400-1000 2000-30 000	*	M_n	*	*	maltenes asphaltenes
[13]	NEWITT E.J. <i>et al.</i> , 1966	4000-35 000	0.5-2% (w/wt)	M_n	10%	*	polyethylene
[14]	JOSE J. <i>et al.</i> , 1972	200-800	0.1-1% (w/wt)	M_n	1-2%	4 h	hydrocarbon compounds, hexamethylphosphorotriamide
[15]	CARBONNEL L. <i>et al.</i> , 1973	600-2500	0.1-1.2% (w/wt)	M_n	1-3%	*	polyesters (polysebacates, polyadipates)
[16]	MOSCHOPEDIS S.E. <i>et al.</i> , 1976	600-10 000	1-15% (w/wt)	M_n	*	*	asphaltenes
[17]	QI YU TAI <i>et al.</i> , 1996	*	*	M_n	10%	*	asphaltenes and petroleum residues

THERMODYNAMIC COLLIGATIVE METHODS (cont'd)

Ref. no.	Techniques and authors	Range of molecular weight (g/mol)	Range of concentration	Type of molecular weight	Experimental uncertainty	Duration of experimentation	Type of macromolecules analysed (asphaltenes, crude fractions, polymers, etc.)
3. VAPOR PRESSURE OSMOMETRY							
[18]	WACHTER A.H. <i>et al.</i> , 1969 (Industrial Tonometry (I. Tono))	600-4.10 ⁵	0.05-7 g/100 cm ³ (benzene)	<i>Mn</i>	1-10%	*	polystyrenes
[16]	MOSCHOPEDIS S.E. <i>et al.</i> , 1976 (I. Tono)	1000-5000	2-7% (w/wt)	<i>Mn</i>	*	*	asphaltenes (bituminous petroleum)
[19]	SCHWAGER I. <i>et al.</i> , 1977 (I. Tono)	300-650	4-36 g/l (benzene)	<i>Mw</i>	0.5-6%	*	coal-derived asphaltenes
[20]	LARSEN J.W. <i>et al.</i> , 1979 (I. Tono)	300-4000	200 mg/L (pyridine)	<i>Mn</i>	2-20%	*	Bruceton depolymerised coal
[21]	BRIANT J. <i>et al.</i> , 1983 (I. Tono)	1000-10 000	5-55 g/l (%C ₆ H ₆ + % nC ₇)	<i>Mn</i>	5-20%	*	asphaltenes
[22]	MRKVILAKOVA L. <i>et al.</i> , 1985 (I. Tono)	< 35 000	*	<i>Mn, Mw</i>	*	*	PS-MTBE, POE-CH, PIB-CH
[23]	BLONDEL-TELOUK A., 1995 (real tonometry)	150-1000	5 × 10 ⁻³ -5 × 10 ⁻² (mol/mol)	<i>Mn</i>	2%	4 days	heavy crudes (in benzene)
[24]	STUBINGTON J.F. <i>et al.</i> , 1995 (I. Tono)	300-800	0.2-0.8% (w/wt)	<i>Mn</i>	*	*	shale oils, lubricating oils, maltenes
[25]	COUTINHO F.M.B. <i>et al.</i> , 1996 (I. Tono)	800-6000	*	<i>Mn</i>	1%	*	urethane-based anionomers (chloroform)
4. OSMOMETRY (OSMOTIC PRESSURE OR MEMBRANE OSMOMETRY)							
[26]	ATTWOOD D., 1969	*	*	<i>Mn</i>	5% /light scattering (<i>Mw</i>)	*	cetomacrogol 1000
[27]	ATTWOOD D., 1970	15 000-70 000 10 000-80 000	30-60 g/l (water) 10-40 g/l	<i>Mn</i>	3%	1-2 h	<i>n</i> -dodecyl hexaoxyethylene monoether, <i>n</i> -hexadecyl nonaoxyethylene monoether, <i>n</i> -cetyltrimethylammonium bromide
[28]	COLL H., 1970	17 000-35 000	0.18-0.9 g/l (water)	<i>Mn</i>	2-3%	1-2 h	sodium dodecyl sulfate in aqueous sodium chloride solutions
[16]	SPEIGHT J.G. <i>et al.</i> , 1976	80 000	*	<i>Mn</i>	*	*	asphaltenes
[29]	SAITO M., 1983	2.7 × 10 ⁴ -7.2 × 10 ⁴	*	<i>Mn</i>	*	*	cellulose acetate
[30]	FULLERTON G.D. <i>et al.</i> , 1993	65 000-69 000	6-10% (w/wt)	*	0.9-2.5%	2-4 h	bovin serum albumin
5. VISCOSIMETRY							
[35]	ECKERT G.W. <i>et al.</i> , 1947	1400-1700	2-9 g/l	<i>Mw</i>	large error: <i>Mn</i> > <i>Mw</i>	*	asphaltenes
[36]	REERINK, 1973 (+ ultracentrifugation)	5 000-50 000	*	<i>Mw</i>	*	*	asphaltenes
[16]	MOSCHOPEDIS <i>et al.</i> , 1976	100-1100	0.1-1% (w/wt) 3-17% (w/wt)	<i>Mw, Mn</i>	3-24% > 100%	*	naphthalene, biphenyl, asphaltenes
[21]	BRIANT J., 1983	7000	4-25 g/l (benzene)	<i>Mn</i>	> 5%	*	asphaltenes
[37]	KAMIDE K. <i>et al.</i> , 1986	3.1 × 10 ⁴ -11.5 × 10 ⁴	3-10% (w/wt)	<i>Mw</i>	idem light scattering	*	celluloses in aqueous lithium hydroxyde solutions
[38]	TESTERECI H.N. <i>et al.</i> , 1995 (+ light scattering)	1.4 × 10 ⁵ -8.5 × 10 ⁵	0.01-0.04 g/l (water)	<i>Mw</i>	5%	5 h	polyadenylic acid
[39]	LU S.X. <i>et al.</i> , 1997	3 × 10 ⁴ -9.1 × 10 ⁴	*	<i>Mw</i>	*	*	amorphous poly (phenylene sulfide)

SEPARATION METHODS

Ref. no.	Techniques and authors	Range of molecular weight (g/mol)	Range of concentration	Type of molecular weight	Experimental uncertainty	Duration of experimentation	Type of macromolecules analysed (asphaltenes, crude fractions, polymers, etc.)
6. SIZE EXCLUSION CHROMATOGRAPHY (SEC) or GEL PERMEATION CHROMATOGRAPHY (GPC)							
[40]	HALEY <i>et al.</i> , 1971-1975 SEC/tonometry and SEC/osmometry	200-400	*	<i>M_n</i>	*	*	asphaltenes
[41]	REERINK <i>et al.</i> , 1975	10 000-3×10 ⁵	*	<i>M_n</i>	*	*	asphaltenes
[42]	GOURLAOUEN C., 1984	45 000-90 000	*	<i>M_w</i>	*	*	asphaltenes
[43]	RODGERS <i>et al.</i> , 1987	100-500	*	<i>M_n</i>	3.6-10%	*	eicosane, squalane, cyclohexane, coronene
[44]	ROSSET R. <i>et al.</i> , 1994 SEC-viscosimetry + refractometry (universal calibration) and SEC-IR	200-10 ⁶	0.2 g/l-0.003 g/ml	<i>M_n, M_w</i>	1-7%	1 h	polystyrenes, polyisobutenes
[45]	AZUMA C. <i>et al.</i> , 1995 SEC-universal calibration	10 000-160 000	*	<i>M_w, M_n</i>	*	*	acrylonitrile polymers, PEO, PS in DMF
[46]	HARRISON C.A. <i>et al.</i> , 1995 SEC-refract. (DRI), SEC-UV, SEC-differential viscosimetry (DV), SEC- DRI /DV	250-3200	2,5 mg/ml (phenyl isocyanate, methanol, hexanol)	<i>M_n</i>	< 3% (9% max) < 3% 12-20% < 8%	1 h	poly(tetramethylene glycol)
[47]	KONAS M. <i>et al.</i> , 1995 SEC-universal calibration	5000-70 000	1-2.5 mg/ml (THF)	<i>M_w, M_n</i>	3-8%	*	polyimides
[24]	STUBINGTON J.F. <i>et al.</i> , 1995 SEC-differential refractometry	300-800	0.2-0.8%	<i>M_n</i>	*	1 h	shale oils, lubricating oils, maltenes
[48]	VAN ASTEN A.C. <i>et al.</i> , 1995 SEC-ThFFF (Thermal Field Flow Fractionation)	9000-130 000	1-5 mg/l (THF)	*	*	1 h	polystyrene, polybutadiene, polytetrahydrofuran, butadiene and styrene-methylmethacrylate copolymers
[25]	COUTINHO F.M.B. <i>et al.</i> , 1996	700-11 000	*	<i>M_w, M_n</i>	< 50%/VPO	*	urethane-based anionomers
[49]	DABIR B. <i>et al.</i> , 1996	800-11 000	[solv.]/[unkn.] = 1.5-10	<i>M_w, M_n</i>	*	*	asphaltenes, asphalts
[50]	MORI S. <i>et al.</i> , 1996	*	*	<i>M_w</i>	4%	*	polystyrenes
[51]	POETSCHKE H. <i>et al.</i> , 1996	10 ⁵ -10 ⁶	*	<i>M_w, M_n</i>	2-11%	*	hemoglobine, hyperpolymers
[52]	RADER H.J. <i>et al.</i> , 1996	5000-12 000	*	<i>M_w, M_n</i>	2-8% /MALDI-TOF	*	tetrahydropyrene oligomers
[53]	TRATHNIGG B. <i>et al.</i> , 1996 SEC-RI (Refractive Index) + ELSD (Evaporative Light Scattering Detector) + density	300-500	*	<i>M_w, M_n</i>	< 3%	*	polyethylene glycol (PEG) 300, polypropylene glycol (PPG) 425 in CHCl ₃ , in water and in THF
7. SUPERCRITICAL FLUID CHROMATOGRAPHY (SFC)							
[54]	HIRATA Y. <i>et al.</i> , 1984 SFC-UV	580 - 9000	0-20% (THF)	<i>M_w</i>	*	2-3 h	polystyrene standards
[55]	ESCOTT R.E.A. <i>et al.</i> , 1991 SFC-FID	200-800	*	*	*	< 30 min	PEG 200 to 4000, methoxy PEG 2000, M-PEG
[56]	HOLZBAUER H.R. <i>et al.</i> , 1994 SFC-FID	500-600	*	<i>M_w, M_n</i>	0.3%/VPO < 10%/GPC, SEC	1-2 h	PEG 600
[57]	JUST U. <i>et al.</i> , 1994 SFC-FID	< 1000	*	<i>M_w</i>	*	> 1 h	oligomeric ethylene oxide adducts
[58]	TAKEUCHI M. <i>et al.</i> , 1996 SFC-ELSD + UV	2000	*	<i>M_w</i>	*	*	PEG 2000, PPG 2000
[53]	TRATHNIGG B. <i>et al.</i> , 1996 SFC-FID	300-500	*	<i>M_w, M_n</i>	< 3% /MALDI-TOF MS, SEC	*	PEG 300, PPG 425

SEPARATION METHODS (cont'd)

Ref. no.	Techniques and authors	Range of molecular weight (g/mol)	Range of concentration	Type of molecular weight	Experimental uncertainty	Duration of experimentation	Type of macromolecules analysed (asphaltenes, crude fractions, polymers, etc.)
8. LIQUID CHROMATOGRAPHY							
[55]	ESCOTT R.E.A. <i>et al.</i> , 1991 Reversed phase HPLC-UV	200-4500	*	*	*	< 50 min	PEG 200 to 4000, methoxy PEG 2000, M-PEG
[53]	TRATHNIGG B. <i>et al.</i> , 1996 LAC: Reversed phase - density + RI + ELSD	300-500	(methanol)	<i>M_w</i> , <i>M_n</i>	< 3% /MALDI TOF MS	*	PEG 300, PPG 425
[53]	TRATHNIGG B. <i>et al.</i> , 1996 LAC: Normal phase - density + RI + (density + RI)	300-500	(2-propanol/ water)	<i>M_w</i> , <i>M_n</i>	< 3% /MALDI TOF MS	*	PEG 300, PPG 425
9. ULTRACENTRIFUGATION							
[31]	UTIYAMA H. <i>et al.</i> , 1969	1.5×10^5 - 2×10^6	0.15-0.55 g/dl (2-butanone)	<i>M_w</i>	2%	20 h	monodispersed polystyrene
[32]	WANG F.W. <i>et al.</i> , 1983	37 400	0.001-0.005 g/cm ³ (cyclohexane)	<i>M_w</i>	2%	*	polystyrene SRM 1478
[33]	LEMERLE J. <i>et al.</i> , 1984	2500	0.002-0.009% (w/wt)	<i>M_w</i>	*	*	asphaltenes
[34]	BUDD P.M., 1988	10^5 - 10^6	0.0005-0.004 g/cm ³ (toluene)	<i>M_w</i>	12%	> 8 h	polystyrene 706
10. FIELD FLOW FRACTIONATION (FFF)							
[59]	LEE S., 1992 (Thermal-FFF)	3×10^5 - 6×10^6 2×10^5 - 1×10^6	* *	<i>M_w</i> , <i>M_n</i> <i>M_w</i> , <i>M_n</i>	* 10-70% /SEC-RID, SEC-viscosi. SEC-LS	* *	polymethylmetacrylate (PPMA) acrylate elastomers
[60]	MYERS <i>et al.</i> , 1992 (Thermal-FFF)	$15\ 000$ - 1.05×10^6	0.1% (w/wt)	<i>M_w</i> , <i>M_n</i>	< 5%	*	linear polystyrene standard
11. ULTRAFILTRATION							
[61]	GREGOR H.P. <i>et al.</i> , 1978	100-70 000	*	<i>M_w</i>	*	*	erythosine albumin, sucrose
[62]	SPEIGHT J.G. <i>et al.</i> , 1985	80 000-140 000	*	<i>M_w</i>	*	*	asphaltenes
[63]	OHYA H. <i>et al.</i> , 1997 (polyimide aromatic membrane)	170-400	*	<i>M_w</i>	*	*	gasoline/kerosine mixture

SPECTROSCOPIC METHODS

Ref. no.	Techniques and authors	Range of molecular weight (g/mol)	Range of concentration	Type of molecular weight	Experimental uncertainty	Duration of experimentation	Type of macromolecules analysed (asphaltenes, crude fractions, polymers, etc.)
12. SPIN COATING							
[64]	SCHUBERT D.W., 1997	10^5 - 7×10^5	5-25 g/l (toluene)	*	< 15%	*	polystyrene
13. NUCLEAR MAGNETIC RESONANCE (NMR)							
[65]	SPYROS A. <i>et al.</i> , 1997 ³¹ P NMR	13×10^4 - 5×10^5	50-100 mg/mL (CDCl ₃)	<i>M_n</i>	10-25% /GPC < 30% /viscosimetry	*	poly(hydroxyalkanoates)

SPECTROSCOPIC METHODS (cont'd)

Ref. no.	Techniques and authors	Range of molecular weight (g/mol)	Range of concentration	Type of molecular weight	Experimental uncertainty	Duration of experimentation	Type of macromolecules analysed (asphaltenes, crude fractions, polymers, etc.)
14. LIGHT SCATTERING (LS)							
[66]	DUCOURET G., 1987 Small Angle Neutron Scattering (SANS)-GPC	33 000-77 000	1% (THF)	*	*	*	asphaltenes
[67]	GOTTIS P.G. <i>et al.</i> , 1989 Infrared LS 1064 nm (Rayleigh scatt.)	4000-134 000	0.1-4 g/l (orthoxylyene)	<i>Mn</i>	20%	*	asphaltenes
[68]	HERZOG P., 1990 SA X-ray S SANS SANS SANS	42 000 44 300 20 000-140 000 30 000-300 000	1% (orthoxylyene) 1% (orthoxylyene) 1% (TDF, pyridine, C ₆ D ₆ , orthoxylyene, toluene) 0.1-8% (benzene/orthoxylyene)	* * * *	* * * *	* * * *	asphaltenes asphaltenes asphaltenes asphaltenes
[69]	ESPINAT D. <i>et al.</i> , 1984-86 Central X-ray scattering	4000-134 000	6-10% (w/wt)	<i>Mn</i>	10% /tonometry	*	asphaltenes
[70]	ESPINAT D., 1991 SAXS and SANS	16 000-89 000	0.7-1.2% (pyridine, benzene, etc.)	<i>Mw</i>	*	*	asphaltenes
[71]	BERTH G. <i>et al.</i> , 1994 Static laser LS 632.2 nm	30 000-7×10 ⁷	*	<i>Mw</i>	*	*	high methoxyl citrus pectin
[72]	CHI WU <i>et al.</i> , 1994 Dynamic laser L.S. 488 nm	30 000-300 000	4×10 ⁻⁴ - 8×10 ⁻³ g/ml (chloroform or THF)	<i>Mw</i>	*	*	segmented copolymers of polyethylene-terephthalate-co-caprolactone
15. MASS SPECTROSCOPY (MS)							
[73]	UDSETH H.R. <i>et al.</i> , 1977 (flash desorption) + EI (Electronic Impact)/ CI (Chemical Ionisation)-MS	2100	*	<i>Mn</i>	5.4%	*	polystyrene
[74]	LATTIMER R.P. <i>et al.</i> , 1980	500-3500	*	<i>Mn</i>	< 2%	*	polystyrene
[75]	LATTIMER R.P. <i>et al.</i> , 1981 FD (Field Desorption)-MS	400-3000 < 11 000	*	<i>Mn, Mw</i>	< 5-6% *	*	PPG, PEG, PTHF, polystyrene
[76]	LATTIMER R.P. <i>et al.</i> , 1983 FD-MS	< 10,000	*	<i>Mn</i>	5%	*	polybutadiene, polyisopropene, polyethylene
[77]	MATTERN D.E. <i>et al.</i> , 1985	400-1000	*	<i>Mn</i>	2%	*	polyglycols (PEG, PPG)
[78]	BROWN R.S. <i>et al.</i> , 1986 LD (Laser Desorption)- FT MS	< 6000	5 mg/ml (methanol)	<i>Mn, Mw</i>	*	*	P.E.G 600 to 6000, PPG, PEI, polystyrene, polycaprolactone-diol
[79]	COTTER R.J. <i>et al.</i> , 1986	< 5000	1 mg/ml (methanol)	<i>Mn, Mw</i>	< 4% /LD-FT-MS, EGT, FD-MS, FAB-MS, EH-MS	*	PEG (1450, 3350), PPG (790, 1220, 2020, 3000), PEI (600, 1200, 1800)
[86]	BOUQUET M. <i>et al.</i> , 1990	200-450	*	<i>Mw</i>	3-7.5% < 6% /GC	*	heavy hydrocarbon cuts
[80]	ZUBAREV R.A. <i>et al.</i> , 1995 Plasma desorption - TOF MS	< 10 000 > 10 000	*	<i>Mw</i>	0.1 Da 10 ppm	*	biomolecules (bovin insuline)
[52]	RADER H.J. <i>et al.</i> , 1996 MALDI - TOF MS	5000-12 000	*	<i>Mn, Mw</i>	2-8% /GPC (THP calibration)	*	tetrahydropyrene oligomer (THP)
[53]	TRATHNIGG B. <i>et al.</i> , 1996 MALDI - TOF MS	300-500	*	<i>Mn, Mw</i>	< 3% /SEC, SFC, LAC	*	PEG 300, PPG 425

PART 2 – EBULLIOMETRIC MEASUREMENT OF MOLECULAR WEIGHT

2.1 Purpose of this Study and Choice of the Method

As has been previously shown [82], the current industrial equipment, i.e. VPO, provides the most reliable results for the measurement of molecular weight of petroleum fractions. However, in the case of heavy fractions, the experimental uncertainty becomes significant (about 10%), even for molecular weights below 1000 g/mol [18] and [23].

Given this fact, which has been known for some time, studies have been carried out to find a more accurate way to measure molecular weight. Among these studies is the work of A. Blondel-Telouk in 1994 [23] on a static differential tonometer. This original apparatus led to accurate results for the number average molecular weight (Mn) of crude oils, with an uncertainty of about 2%. The accuracy goal was reached, but the measurement time was too long for a routine technique, i.e., 4 days/ Mn .

This important notion of measurement duration was a motivation for our work. We had to determine in the same range of molecular weights (**150-1000 g/mol**), **the number average molecular weight (Mn)** of heavy crude fractions with, at least, the same accuracy ($\Delta Mn/Mn \leq 2\%$) but with a measurement time **inferior to 4 days**.

The colligative thermodynamic methods, i.e., methods where the studied properties of the solution depend on the concentration of the added sample, like VPO, cryometry, ebulliometry, osmometry and tonometry are well-known for measuring Mn . They give reliable results for this type of molecular weight, even if they are very sensitive to sample purity [62].

Among the other techniques for measuring Mn , if we take industrial constraints into account (cost, measurement time and simplicity), the GPC (or SEC) method has been successfully used in the petroleum industry over the last 20 years [40, 41, 42, 49, 83], even though some of the problems of detection, calibration/correction and plugging of the column persist. The rise of SFC in the last 10 years is also to be noted [53] and [58].

Although well equipped for chromatographic analysis techniques, our laboratory has a long experience in colligative thermodynamic methods.

In order to reduce the measurement time, we decided to choose a **dynamic thermodynamic method**, as opposed to the static-differential tonometer [23] which requires a long degassing step. Laboratory experience in cryometric and tonometric measurements [12] and [23] shows the difficulty of applying these techniques for our purpose. Consequently, we chose the **ebulliometric method**.

2.2 Ebulliometry

Principle of the ebullioscopic measurement of Mn

Ebulliometry is based on the increase of the boiling temperature of a solvent after adding a solute. Thus, by measuring the difference between the boiling point before and after adding the solute and by using the basic ebulliometric relation (Eq. (1)) (see below) it is possible to deduce the number average molecular weight.

$$\overline{Mn} = K_{eb} \frac{C}{\Delta T_{eb}} \quad (1)$$

with:

$$\overline{Mn} = \frac{\sum_i n_i M_i}{\sum_i n_i} \quad (2)$$

number average molecular weight

K_{eb} ebulliometric constant

$$\frac{R \times T_{eb}^2 \times M}{1000 \times \Delta H_e} = 3.402 \text{ g mol}^{-1} \text{ K} \quad (3)$$

C solute concentration in g/1000 g of solvent

ΔT_{eb} boiling points difference in °C or K

T_{eb} solvent boiling point (383.75 K for toluene)

M molecular weight of the solvent (92.15 g/mol for toluene)

ΔH_e vaporization enthalpy of the solvent (33.1641 kJ/mol for toluene)

R perfect gas constant = 8.314 J mol⁻¹ K

M_i molecular weight of the compound i in the solute

n_i number of moles of the compound i in the solute.

The ebullioscopic Equation (1) is only valid for very dilute solutions, which is the case here. For more concentrated solutions, a C^2 term is required [88].

By plotting ΔT_{eb} as a function of concentration C , we obtain a straight line. Its slope is calculated with the

classical least squares method which consists of minimizing the quantity:

$$\frac{\sum (\Delta T_{eb\ exp} - \Delta T_{eb\ calc})^2}{i}$$

where:

$\Delta T_{eb\ exp}$ experimental boiling point variation

$\Delta T_{eb\ calc}$ calculated boiling point variation (using Eq(1))

i number of experimental points.

This simple method is justified by the fact that the experimental uncertainty in C , which comes from the weighing ($\Delta C/C < 0.001\%$) is largely negligible compared to the measurement errors in ΔT_{eb} due to the method itself. In effect, although the micro-voltmeter allows a measurement of ΔT_{eb} to about

$\pm 0.002^\circ\text{C}$ (i.e., a relative uncertainty in ΔT_{eb} of about $\pm 0.0005\%$), we obtain, in the best case, an experimental uncertainty in the average molecular weight of 0.06%. This error is greater than that which we might deduce from the propagation of errors (Eq. (1)). This means that factors related to the experimental method itself, such as slight thermal gradients, weak variations in the composition C due to vaporization, etc., affect the accuracy of ΔT_{eb} .

2.3 A Comparative Ebulliometer for the Measurement of M_n of Heavy Crude Fractions

2.3.1 General diagram of the apparatus (fig. 1)

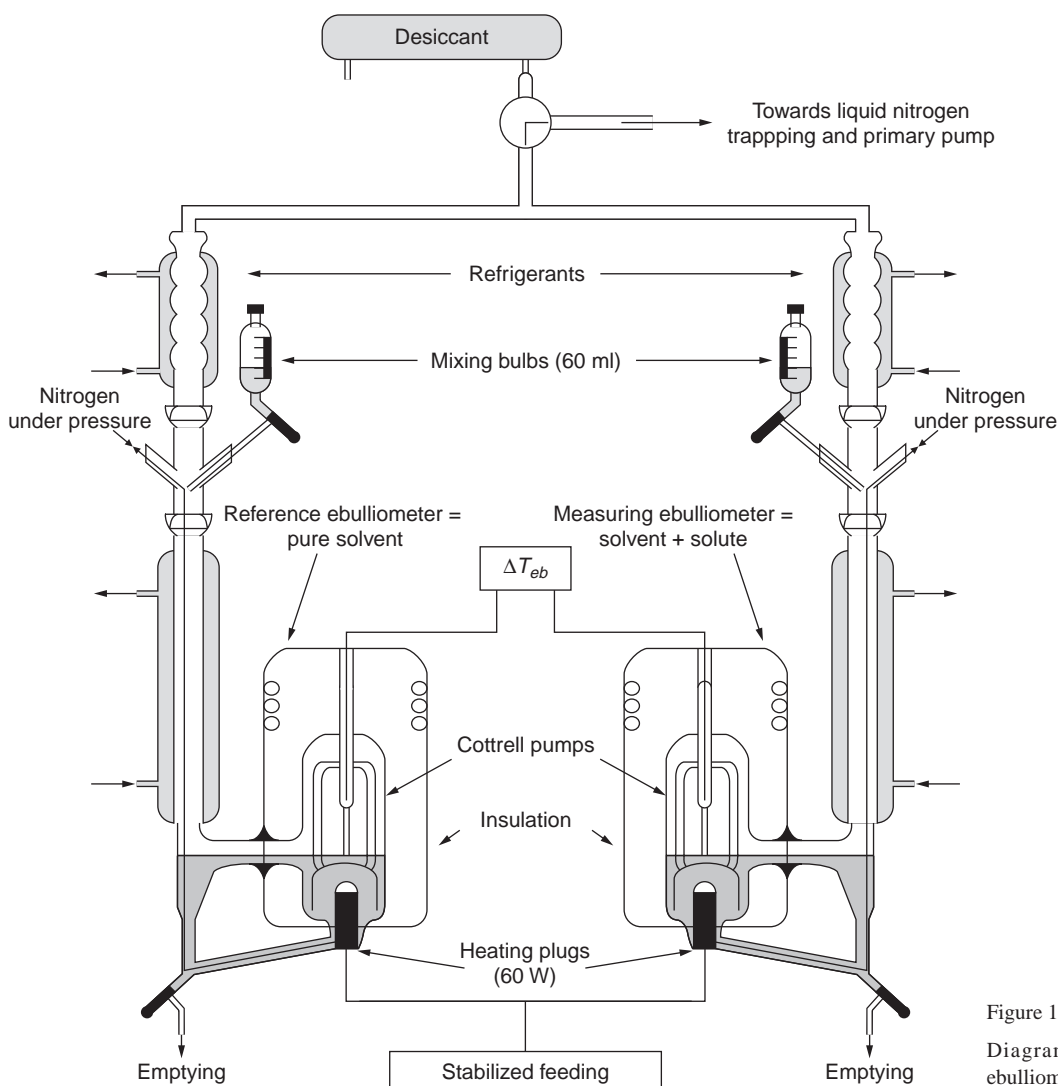


Figure 1
Diagram of the comparative ebulliometer.

2.3.2 Description

A single glass ebulliometer had been designed and manufactured at *IFP*. Using it as a starting point, we designed and manufactured a "twin apparatus" from two identical "IFP-type" ebulliometers. In this way, we obtained a comparative ebulliometer. One ebulliometer is for the measurements and the other one is used as a reference.

A heating plug with a stabilized power supply brings the solvent to its boiling point. Ebullition is regulated by an internal flow of nitrogen and by little pieces of powdered glass stuck on the internal walls of the boiler.

To measure the "true" boiling point, the measuring point should be between the liquid and vapor phases at equilibrium. This is achieved with three Cottrell pumps, disposed at 120° from each other, that alternately bring vapor and liquid to the measuring point.

The temperature difference, ΔT , is measured with a single-junction Copper/Constantan thermocouple welded with silver and is recorded with a microvoltmeter. The sensitivity of the thermocouple is 40 mV/°C. The weld areas are immersed in an oil bath that permits thermal absorption while eliminating the need to use mercury. The whole "measuring cell" is placed in a fine glass tube.

The vapors are condensed by two water refrigerants in series. Vapor and liquid are mixed before returning to the boiler.

The circulation of the liquid is obtained due to the form of the elbow, which generates a natural thermosiphon.

Thermal insulation is obtained by means of a silver coating on the external envelope, which is under vacuum. A higher degree of insulation is achieved by an external jacket surrounding the whole apparatus.

The apparatus works in a dry atmosphere obtained with a desiccant placed at its top. The ebulliometers can be emptied by means of a primary pump which generates a reduced pressure in the whole apparatus. This primary pump is protected with a nitrogen trap.

The sensitivity of the measured temperature is $\pm 0.0021^\circ\text{C}$.

This apparatus presents some advantages: simple operation, short duration of equilibrium (1 hour), efficient vapor condensation, no variation of composition during the running time, good internal circulation of vapor and liquid (i.e. no accumulation

zones), good mixing of fluids before their return to the boiler.

Variation in the composition was checked by FID-gas chromatography. Several samples were extracted from the running liquid in different parts of the ebulliometer. The observed differences of composition were very small, thus not significant and due to experimental uncertainties [13].

2.3.3 Calibration and operating procedures [11]

We studied three methods for making measurements.

The first method is called the "accurate method". The experiments are carried out with four concentrations that are prepared and measured independently.

The calibration was carried out using seven standards (**Prolabo PA, Purity > 99% + distillation**) in toluene: *n*-decane, 1-methylnaphthalene, *n*-dodecane, diphenyl-methane, *n*-tetradecane, *n*-eicosane and squalane. The fitting of ΔT_{eb} as a function of C (Eq. (1)) allows the calculation of the average molecular weight of the solute.

The results of the calibration were satisfying except, for *n*-decane and *n*-dodecane. Their vapor pressures at 110 °C (toluene boiling point) cannot be neglected: 101 mm Hg for *n*-decane and 22.877 mm Hg for *n*-dodecane. With these vapor pressures, one part of the sample goes into the vapor phase and the liquid composition is modified. The determination of M_n becomes inaccurate. The average accuracy ($\Delta M_n/M_n$) for the five others standards is about **0.06%** in the range 10-50 g/1000 g of solvent. The time for one molecular weight measurement is two days.

The second method is called the "rapid method". The experiments are carried out with six concentrations in order to reduce the experimental uncertainty. This method uses quantified additions, that is, each concentration, except the first, depends on the previous one.

The experiment starts with pure toluene in the two boilers. Then, a sample solution in toluene is added by means of an injection syringe and a specially designed connector, which is placed between the two water-refrigerants.

The calibration was carried out with five standards: 1-methylnaphthalene, diphenylmethane, *n*-tetradecane, *n*-eicosane and squalane. We observed that with this method, the fitting of the experimental results with a relation such as:

$$\Delta T_{eb} = m C + b \quad (4)$$

with $m = K_{eb}/Mn$, provides molecular weights which agree better with the theoretical values than those fitted by the relation $\Delta T_{eb} = m C$. The b term comes from a slight effect of the liquid volume on ΔT_{eb} .

We verified that the addition of a few cm³ of pure solvent to the measurement ebulliometer leads to a variation of ΔT_{eb} of about 0.002-0.006 °C. This variation is especially noticeable after the first addition. This may be due to a weak variation of the thermal transfer or of the flow rate of the thermosiphon.

With this calculation method, the average accuracy for these standards is about **0.5%** in the range 10-50 g/1000 g of solvent. The uncertainty is, thus, ten times greater but remains satisfactory. The time for one measurement was reduced from two days to **3-4 hours**.

Figure 2 illustrates a study on *n*-tetradecane, in the range 10-50 g/1000 g solvent, with this method. In this example, $n = 8$.

The last method, called the “*in situ* method”, requires an internal standard. Figure 3 illustrates this

method. We noticed that it was possible, in the case of non-association phenomena, to follow alternately the behavior of a standard and of a sample. This method is reliable and allows one to follow the behavior of the system during the entire experiment. In the example presented in Figure 3, the “unknown” sample is 1-methylnaphthalene and the standard is *n*-tetradecane. The accuracy is here less than 1%.

The molecular weight was calculated as described previously by fitting Equation (4) for the same reasons. This method can also be useful in the study of interactions between two samples.

2.3.4 General characteristics of the measuring system

Range:

- molecular weight: 150-2000 g/mol,
- concentration: 10-50 g/1000 g of solvent (1 to 5% w/wt);

Study of <i>n</i> -tetradecane									
	$Mn = 198.4 \text{ g/mol}$			$Mn_{exp} = 199.39$			Relative deviation (%) = 0.50		
Concentration (g/1000 g)	10.01	12.73	15.18	17.51	19.81	30.01	40.15	50.25	0.00
dT °C	0.1749	0.2241	0.2626	0.3043	0.3375	0.5179	0.6903	0.8610	
E.m.f. in mV	0.0082	0.0105	0.0123	0.0143	0.0158	0.0242	0.0322	0.0401	
dT °C	0.1749	0.2241	0.2626	0.3043	0.3375	0.5179	0.6903	0.8610	
Trend (calculated values with the least squares method)	0.1751	0.2215	0.2634	0.3031	0.3423	0.5163	0.6893	0.8617	0.0043

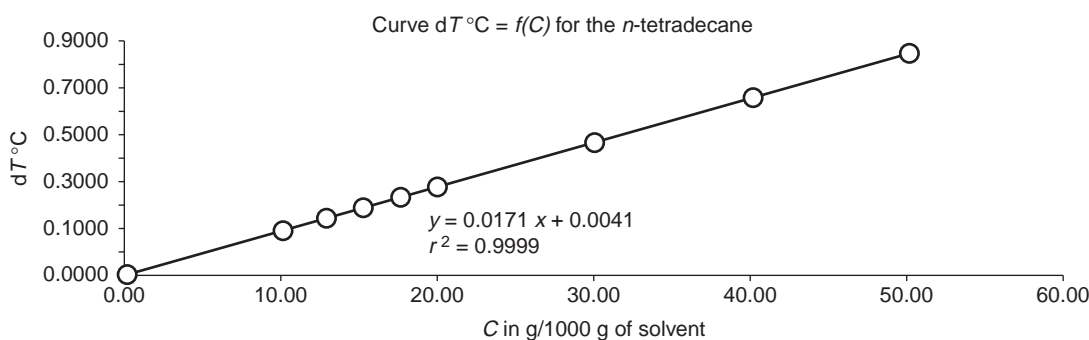


Figure 2
Illustration of the “rapid method”.

Standard: *n*-tetradecane $Mn = 198.4 \text{ g/mol}$ $Mn_{exp} = 197.54$ Relative deviation (%) = -0.43
 Standard: 1-methylnaphthalene $Mn = 142.2 \text{ g/mol}$ $Mn_{exp} = 143.31$ Relative deviation (%) = 0.78

Standard

Concentration (g/1000 g)	10.25	12.13	14.15	16.11	18.11	20.12	0.00
dT °C	0.1685	0.2080	0.2337	0.2701	0.3118	0.3375	
E.m.f. in mV	0.0079	0.0098	0.0110	0.0127	0.0146	0.0158	
dT °C	0.1685	0.2080	0.2337	0.2701	0.3118	0.3375	
Trend (calculated values with the least squares method)	0.1707	0.2029	0.2378	0.2716	0.3060	0.3406	-0.0059

Sample

Concentration (g/1000 g)	10.01	12.09	14.15	15.83	17.92	20.24	0.00
dT °C	0.2283	0.2851	0.03386	0.3665	0.4191	0.4760	
E.m.f. in mV	0.0107	0.0134	0.0159	0.0172	0.0196	0.0223	
dT °C	0.2283	0.2851	0.3386	0.3665	0.4191	0.4760	
Trend (calculated values with the least squares method)	0.2328	0.2822	0.3311	0.3711	0.4207	0.4758	-0.0048

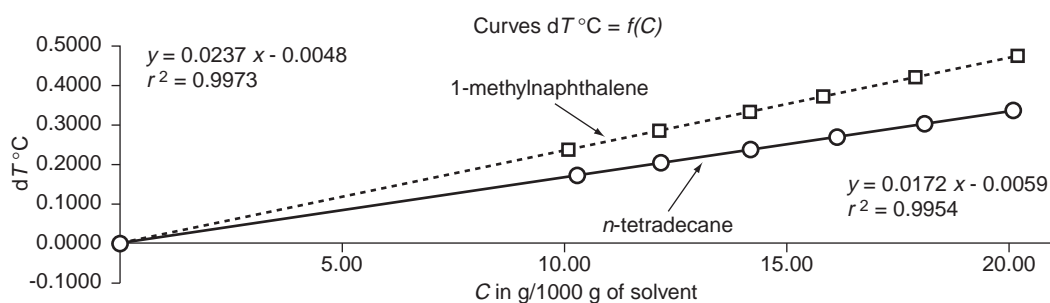


Figure 3
 Illustration of the "in situ method".

Solvent: distilled toluene;
 Temperature sensitivity: 0.0021°C ;
 Accuracy: for pure components:
 - 0.1% with the accurate procedure,
 - 0.5% with the rapid procedure.

2.4 Applications: Measuring the Molecular Weight of Petroleum Fractions - A Preliminary Study

The following studies were made in order to improve the efficiency of our system with real, complex mixtures.

A preliminary experiment with a synthetic mixture of known components was carried out with success and allowed us to undertake studies on petroleum mixtures. Figure 4 shows the results for a synthetic mixture. During the tests, the effect of the heating power on the measurement of ΔT_{eb} was studied.

We have observed that varying the power generates a shift of the curve $\Delta T_{eb} = f(C)$ without significantly changing the slope.

In order to minimize this phenomena, a stabilized power supply ($\Delta V/V < 0.01\%$) was used for the whole experiment.

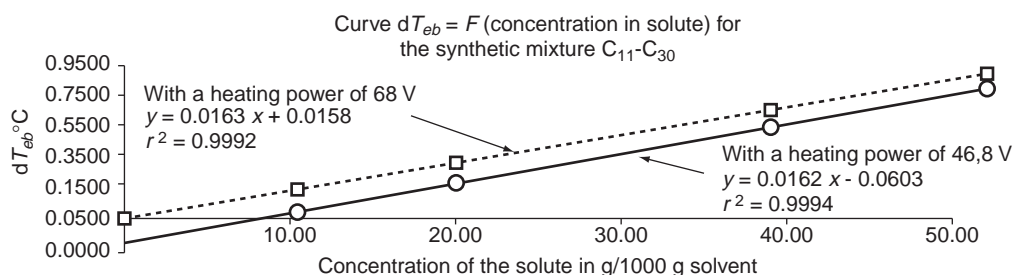
Study of a synthetic mixture C_{11} - C_{30}
Theoretical molecular weight: 210.60 g/mol

Values for the plot $dT = f(C)$ (french relation)

dT °C 46.8 V	0.2594	0.7907	0.5599	0.1119
dT °C 68 V	0.3311	0.8740	0.6428	0.1941
Concentration g/1000 g	19.74	52.21	39.03	10.47

Determination of the molecular weight

	Slope of the straight line	M_n determined	dM_n/M_n in %
68 V	0.0163	208.78	0.86
46,8 V	0.0162	210.50	0.05



Comments:

The relative deviation and the linear regression 46,8 V are satisfactory: the apparatus seems to be reliable for the synthetic mixture that can be assimilated to a pseudo-component in the working range: $150 < M \text{ g/mol} < 450$ and $10 < C \text{ g/1000 g} < 50$.

Mixture	1-methylnaphthalene C_{11}	diphenylmethane C_{13}	tetradecane C_{14}	squalane C_{30}
x (mol, traction)	0.3047	0.2525	0.2781	0.1646

Figure 4

Measurement of the molecular weight of a synthetic mixture.

2.4.1 Preparation of the samples

Small amounts of impurities can considerably modify the results, as shown previously in the literature [7] and [62]. In effect, the number average molecular weight is very sensitive to the compounds present in the mixture.

Thus, we decided to set up a simple distillation apparatus [11] equivalent to a rotative evaporator.

The samples are mixed with toluene which is then evaporated. In this manner, the more volatile impurities are extracted and should not modify the vapor phase composition. Then, the samples are stored in toluene before starting the molecular weight measurement.

2.4.2 Constraints

Small sample quantities compelled us to work within the concentration range 10-25 g/1000 g of solvent rather than 10-50 g/1000 g. For the same reason, we did not want to risk sample contamination, so we chose the rapid method rather than the in situ method, which requires the addition of an internal standard. In this way, the samples could be studied and then recycled for another measurement in case of a problem.

2.4.3 Calibrations

First, we used *n*-tetradecane to verify the efficiency of the new procedure in the concentration range

10-25 g/1000 g of solvent. There were no special problems, and the accuracy was good (< 0.5%).

Then, we worked with distilled squalane to calibrate the equipment and procedure with a heavy component. The accuracy, after ten calibrations with squalane, was found to be about 1%.

2.4.4 Results

Study of three atmospheric residues [84]

We used three atmospheric distillation residue (DV1, DV2, DV3) samples as well as the corresponding cuts obtained by SARA (Saturates, Aromatics, Resins, Asphaltenes) fractionation. Thus, we determined the number average molecular weight of 15 complex mixtures. Because of the high molecular weight of asphaltenes, we were not able to measure them as they are out of the calibration domain. So, the results for asphaltenes were obtained by VPO.

The Table 1 summarizes all the results that were obtained by comparative ebulliometry, except for the molecular weights of the asphaltenes, which were obtained by tonometry.

The repeatability for the whole study, which was estimated with three tests made with the resins, is 1%. We wanted to verify these results and so we made the following material balance.

By assuming that there are no association phenomena, we calculated the molecular weight of the maltenes from those of the saturates, the aromatics and the resins. The fractionation procedure allows to write maltenes = resins + aromatics + saturates.

Then, by using the definition of the number average molecular weight (Eq. (2)) it was possible to obtain:

$$Mn_{malt} = \frac{\%malt}{\frac{\%res}{Mres} + \frac{\%aro}{Maro} + \frac{\%sat}{Msat}} \quad (5)$$

The differences between the observed molecular weights of the maltenes and those calculated by Equation (5) were inferior to 12%.

This deviation is attributed to the experimental uncertainties in the molecular weight measurement, in the composition obtained by the SARA analysis and also to the fact that resins can exhibit a slight association.

Therefore, the results seem to be reliable and the behavior of the apparatus is satisfactory for such experiments.

Study of a resin sample [85]

This example of the efficiency of the comparative ebulliometer concerns the study of resins DV4. These resins were extracted by HPLC from a crude oil. Figure 5 shows one of the six experiments which were performed with this sample. This graph allows us to present another interpretation of the results.

The whole concentration range is divided into two parts: one high concentrations part (HP) which corresponds to the three highest concentrations and one low concentrations part (LP) which corresponds to the three lowest concentrations. This partition was carried out because we systematically observed, in all six experiments a smaller increase in temperature with the addition of the third solute.

The results for the six experiments performed with the same resin sample at different dates are given in Table 2. Between two measurements, the resin sample was stored in a toluene solution.

The results are presented in three columns: one for the molecular weight (MW) over the entire concentration range, one for the MW in the LP and one for the MW in the HP, according to the partition shown above.

TABLE 1

General results for the complete studies of three atmospheric residues

	Saturates	Aromatics	Resins	Maltenes	Atmospheric residue	Asphaltenes
Composition range	33.5-40.6%	35.2-38.7%	15.8-20.4%	91.6-93.6%	100%	6.4-8.4%
DV1	390	500	800	405	430	6100
DV2	380	480	800	470	500	6400
DV3	400	440	640	445	483	5700

DV4: Resins

$Mn_{exp} = 807.86$

Trend = calculated values with the least squares method

Concentration (g/1000 g)	7.88	10.06	12.09	13.95	15.82	17.24	0.00
dT °C	0.0362	0.0469	0.0575	0.0618	0.0703	0.0767	
E.m.f. in mV	0.0017	0.0022	0.0027	0.0029	0.0033	0.0036	
Global trend	0.0374	0.0465	0.0551	0.0629	0.0708	0.0768	0.0042
LP trend	0.0361	0.0471	0.0574	-	-	-	-0.0037
HP trend	-	-	0.0564	0.0634	0.0706	0.0759	-0.0015

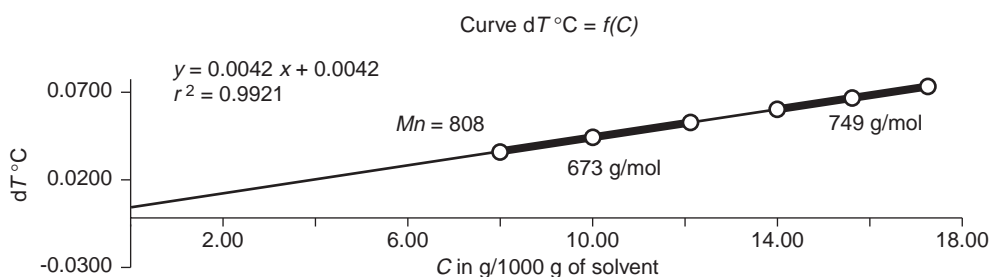


Figure 5

Example of results for the resin sample.

TABLE 2

General results for the resin sample

Test	Date X/10/96	Mn (g/mol) over the whole range	Mn inf on the low conc. part	Mn sup on the high conc. part
1	10	695	668	705
2	11	796	667	746
3	14	714	675	689
4	16	808	673	749
5	17	800	687	773
6	22	707	688	712

Over the whole range of concentrations, when the contact time between toluene and resin is more than 48 hours (tests 1, 3 and 6), the number average molecular weight of the resins is about 700 g/mol with a repeatability of 1%. For a contact time less than 48 hours (tests 2, 4 and 5), the number average molecular weight is about 800 g/mol and the repeatability is also 1%.

The results are quite constant in the lower part of the concentration range. However, in the whole range and in the upper range we observe differences. The search

for variables that could explain these observations led us to take into account the contact time between the solvent and the sample. In effect, we used the same measurement procedure, the same distilled toluene and the same degree of purity for each sample. The only difference is the length of time the resins were stored in the toluene solution. The Figure 6 illustrates more clearly the effect of this parameter.

We can see that for a contact time superior to 48 hours (tests 1,3 and 6), the molecular weights obtained for the upper and whole concentration ranges are almost equal to those for the lower range. However, for a contact time inferior to 48 hours (tests 2, 4 and 5), the former molecular weights are higher than the latter.

As a consequence of the contact time, there are different states of the resins in toluene. If the contact time is long enough or if the solutions are sufficiently dilute, the resin molecules are well dissociated, otherwise they are slightly associated (higher molecular weight). Accordingly, an association threshold, either in duration or in concentration, exists, and the resolution of our ebulliometer is sufficient to detect it.

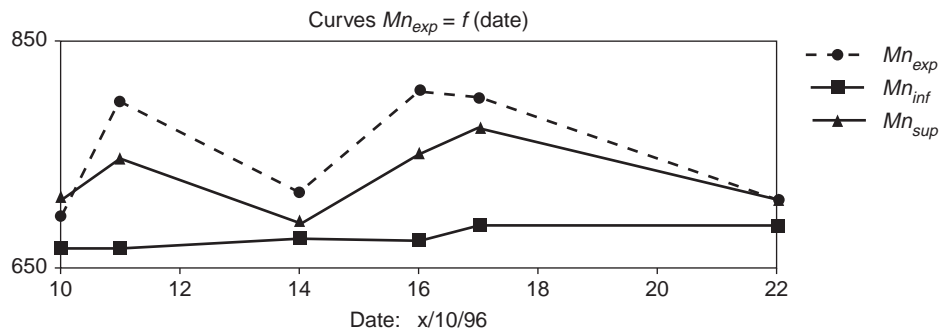


Figure 6

Illustration of the contact time effect.

CONCLUSIONS AND PERSPECTIVES

The behavior of the comparative ebulliometer with heavy petroleum fractions is satisfactory. The uncertainty for such mixtures is estimated to be 2%. The measurement of the number average molecular weight can be performed between 150 and 2000 g/mol with solute concentrations between 10 and 50 g/mol. The measurement lasts less than 4 hours, so the initial objectives were successfully attained. However, the apparatus cannot function outside these ranges, that is, with solid samples or with very dilute solutions, i.e. $C < 1$ g/1000 g of solvent. Moreover, it requires relatively large sample quantities. Hence, in order to undertake the study of macromolecules (asphaltenes, polymers), which requires very dilute solutions, we are compelled to build a new high performance comparative ebulliometer [87]. Our current experience, described above will help us in this future work.

ACKNOWLEDGMENTS

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