DETERMINATION DE LA COURBE DE DISTRIBUTION DU POINT D'EBULLITION DES ESSENCES ET DE SES COMPOSES.

RAPPORT DE STAGE.

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RAPPORT DE STAGE

Méthode d'analyse D-3710 (ASTM) en phase gazeuse

"Détermination de la courbe de distribution du point d'ébullition des essences et de ses composés".

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TABLE DES MATIERES

ANNEXES

I- INTRODUCTION: système CDS 401 - Apple II+ en distillation simulée D-3710.

* On pourra, pour une étude plus poussée du système, consulter les ouvrages suivants:

- "Rapport de travail: Méthode d'analyse ASTM D-2887" par Richard Lemieux.
- "Vista 401 Training course manual".
- "Vista 401 Chromatography Data System".
- "Vista Series Gas Chromatography System".

a) La méthode d'analyse ASTM D-3710 sert à déterminer la courbe de distribution du point d'ébullition des essences et de ses composés. Ladite méthode requiert un point d'ébullition final égal ou inférieur à 230^{0}C.

b) Le GC est au coeur du processus, puisqu'il sert à séparer les composants de l'échantillon selon leur point d'ébullition (colonne chromatographique non polaire). Cette séparation nécessite une hausse linéaire et reproductible de la température de la colonne. On détermine la distribution du point d'ébullition en mesurant l'aire sous la courbe ainsi enregistrée, et en la ramenant sur l'axe "Temps de rétention" de la courbe de calibration.

On aura auparavant construit une courbe de calibration en injectant un standard à la composition quantitativement connue couvrant le domaine des Temps de rétention de l'échantillon analysé.

Ce standard doit contenir au moins un composant de point d'ébullition égal ou inférieur au point initial de l'échantillon, et au moins un point d'ébullition égal ou supérieur au point final dudit échantillon[1].

On obtiendra ainsi une courbe du point d'ébullition versus le Temps de rétention, nécessaire à la détermination de la distribution désirée[2].

c) Le système CDS 401 compile les Temps de rétention, calcule les facteurs de réponse relative, soustrait la ligne de base - anihilant ainsi l'interférence due aux émanations de la colonne (bleeding), et transmet les résultats d'intégration et les résultats calculés au Apple II+.

d) Le Apple II+ compile ces résultats, calcule les facteurs de réponse relative pour n-C_3, i-C_4 et n-C_4, et détermine la distribution recherchée[2].

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[1] L'omission de cette condition amène une extrapolation mathématique des points d'ébullition au-delà de la limite du standard, et ainsi des valeurs moins significatives.

[2] Voir section III pour la méthode de calcul utilisée.

II- D-3710 versus distillation traditionnelle:

La méthode ASTM traditionnelle, D-86, détermine la distribution du point d'ébullition par distillation atmosphérique. Une telle opération implique des manipulations volumétriques et des pertes par évaporation spontanée, facteurs introduisant des paramètres variant, parfois d'une façon significative, d'une analyse à l'autre.

La méthode D-3710, par un contrôle plus suivi des conditions expérimentales, offre une meilleure reproductibilité des résultats, des manipulations presqu'inexistantes, sans parler des possibilités d'automatisation (autosampler).

De tels résultats requièrent cependant des conditions d'opération du GC optimales, un traitement des mesures adéquat, tenant compte notamment de la réponse relative du détecteur employé selon la nature même des composés.

III Traitement des données dans D-3710

* Cette tâche est accomplie par le logiciel du système.

Il est cependant indiqué d'en comprendre les fondements.

a) Mesure de l'aire sous la courbe:

Le détecteur en place sur le GC envoie continuellement un signal d'amplitude variable. Le CDS 401, à tous les 50 nSec., fait la moyenne des signaux reçus pendant cet intervalle et la convertit en signal digital, apte à subir les traitements numériques subséquents. Il groupe ces lectures digitales en ensembles de grandeur variable. Le rôle du paramètre "WI" est de déterminer le nombre de lectures qui y seront groupées.

En bref, le CDS 401 stocke des valeurs d'aire en µV x nSec. De ces valeurs sera soustraite l'aire de la ligne de base, construite au préalable.

b) Ligne de base:

Lors de la construction d'une ligne de base, les valeurs d'aire, relevées lors d'une analyse sans injection d'échantillon ("blank run") sont stockées dans la section 11 de la méthode utilisée. Lors des analyses subséquentes, le CDS 401 soustraira de l'aire envisagée, les valeurs contenues dans ladite section. On élimine ainsi les erreurs quantitatives de calcul d'aire dues, par exemple, à une variation indue du signal du détecteur ou au "bleeding" de la colonne. Ce traitement numérique n'élimine cependant pas les variations de signal dues à l'encrassement du détecteur ou à une fuite au niveau du septum du port d'injection.

A noter que le CDS 401 n'effectue pas cette soustraction instantanément, à l'entrée du signal du détecteur. Il stocke ces valeurs, inaltérées, en mémoire ou sur disquette. Une modification ultérieure du chromatogramme en mode "recalculate" est donc possible par altération de la section 11 (pics indésirables, etc...).

c) Détermination des Temps de rétention.

Une fois les paramètres fondamentaux optimisés (paramètres instrumentaux du GC, voir listing D-3710 ("Calib-RT(1)") en annexe), l'étape suivante consiste à injecter, en mode learn, le standard de référence à cet effet (standard RT). Le CDS 401 détermine les Temps de rétention, les valeurs de WI et autres - soit la section 2 de la méthode -. On vérifie ensuite la reproductibilité des Temps de rétention en réinjectant à quelques reprises, dans les mêmes conditions.

Notons au passage que l'injection, en mode learn du standard RT, entraîne l'altération des valeurs de range (= .5) et d'atténuation (= 64) du détecteur vers des valeurs optimisées (range = .05 et atténuation = 1024), mais entraînant du même coup un bruit de fond trop considérable. Il faut donc veiller, après chaque calibration dans ce mode, à rétablir les valeurs initiales.

Ces injections s'effectuent sans transmission des résultats au Apple II+ (voir section 7 de la méthode). Il faut au préalable identifier les pics du standard, de n-C_3 à n-C_{17}. Une fois cette condition remplie, en s'assurant qu'aucun pic étranger n'est détecté dans le standard (on peut les éliminer, si besoin est, par les commandes II, PR, SR ou SN), on transmet, en mode recalculate, ces résultats au Apple 11+ (on aura pris soin de stocker sur disquette la dernière calibration jugée satisfaisante). Ce dernier entrera dans son tableau le Temps de rétention correspondant à chaque pic identifié.

Note: Concernant l'utilisation du Apple 11+, il faut vérifier, selon les unités de température utilisées (^{0}C ou ^{0}F), que les valeurs de points d'ébullition dans le Tableau du Apple 11+ correspondent aux unités voulues (consulter à cet effet les listings concernés). En outre, il faut voir à ajouter ".A" à la suite du nom des aromatiques dans ce tableau, car les calculs considèrent les aromatiques différemment.

d) Calcul des facteurs de réponse relative (RRF).

Au préalable, il faut apporter les changements voulus aux pages 1 et 2 de la section 1, ainsi qu'à la section 7. Dans la section 3, effacer du tableau des pics (p.2) les pics des n-C_3, i-C_4 et n-C_4, ces composés étant absents du standard RRF. Le pic standard n-C_7 devient donc le 6e (page 1, section 3), auquel on affuble le facteur 1, à tous les autres, le facteur 0. Puis on entre les quantités, de i-C_5 à n-C_{17}, en % V/V.

L'injection subséquente du standard RRF entraîne le calcul, par le logiciel du CDS 401, des RRF de i-C_5 à n-C_{17} et celui par le logiciel du Apple 11-, des RRF des n-C_3, i-C_4 et n-C_4.

- Traitement numérique:

  * Toutes les aires considérées sont corrigées (= aire totale - aire ligne de base).

a) Calcul des RRF pour i-$C_5 \longrightarrow$ n-C_{17}:

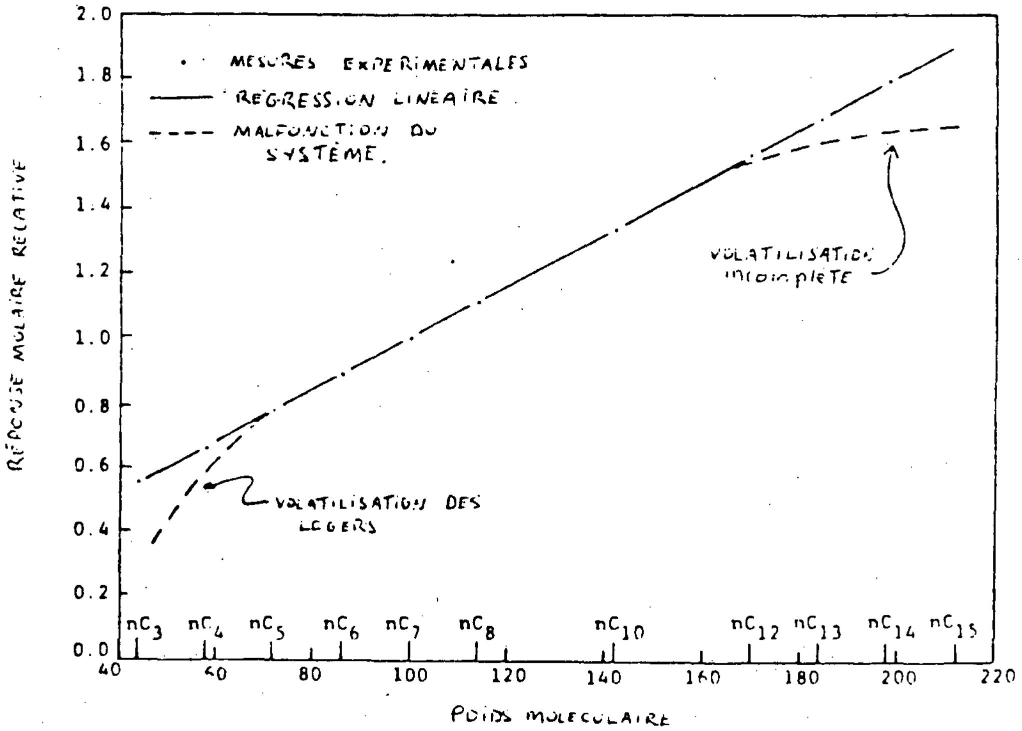
$$\text{RRF: } = \frac{\text{\% vol./vol. du composé:}}{\text{aire du composé:}} \times \frac{\text{aire de n-}C_7}{\text{\% vol./vol. de n-}C_7}$$

b) Calcul des RRF pour n-C_3, i-C_4 et n-C_4:

1^0) Calcul de la réponse molaire relative (RMR) pour i-$C_5 \longrightarrow$ n-C_{17}

$$\text{RMR: } = \frac{\text{aire du composé:}}{\text{\% molaire du composé}} \times \frac{\text{\% molaire de n-}C_7}{\text{aire du n-}C_7}$$

2^0) régression linéaire de la fonction RMR versus poids moléculaire:



3°) Calcul du RMR de $n\text{-}C_3$, $i\text{-}C_4$ et $n\text{-}C_4$:

- à partir de:

  $RMR = a\ MW + b$ (a,b = constantes)

4°) Calcul de RRF: pour $n\text{-}C_3$, $i\text{-}C_4$ et $n\text{-}C_4$:

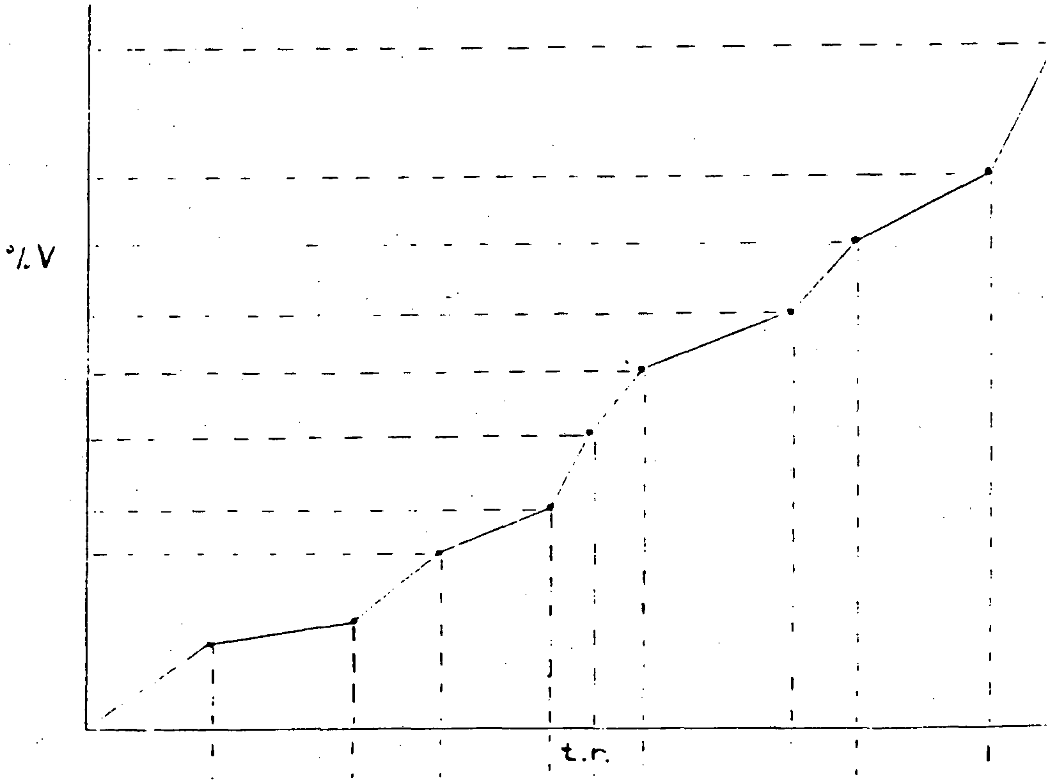
$$RRF: = \frac{\text{MW du composé:}}{\text{MW de } n\text{-}C_7} \times \frac{\text{RMR de } n\text{-}C_7}{\text{RMR du composé:}} \times \frac{\text{densité relative de } n\text{-}C_7}{\text{densité relative du compos}}$$

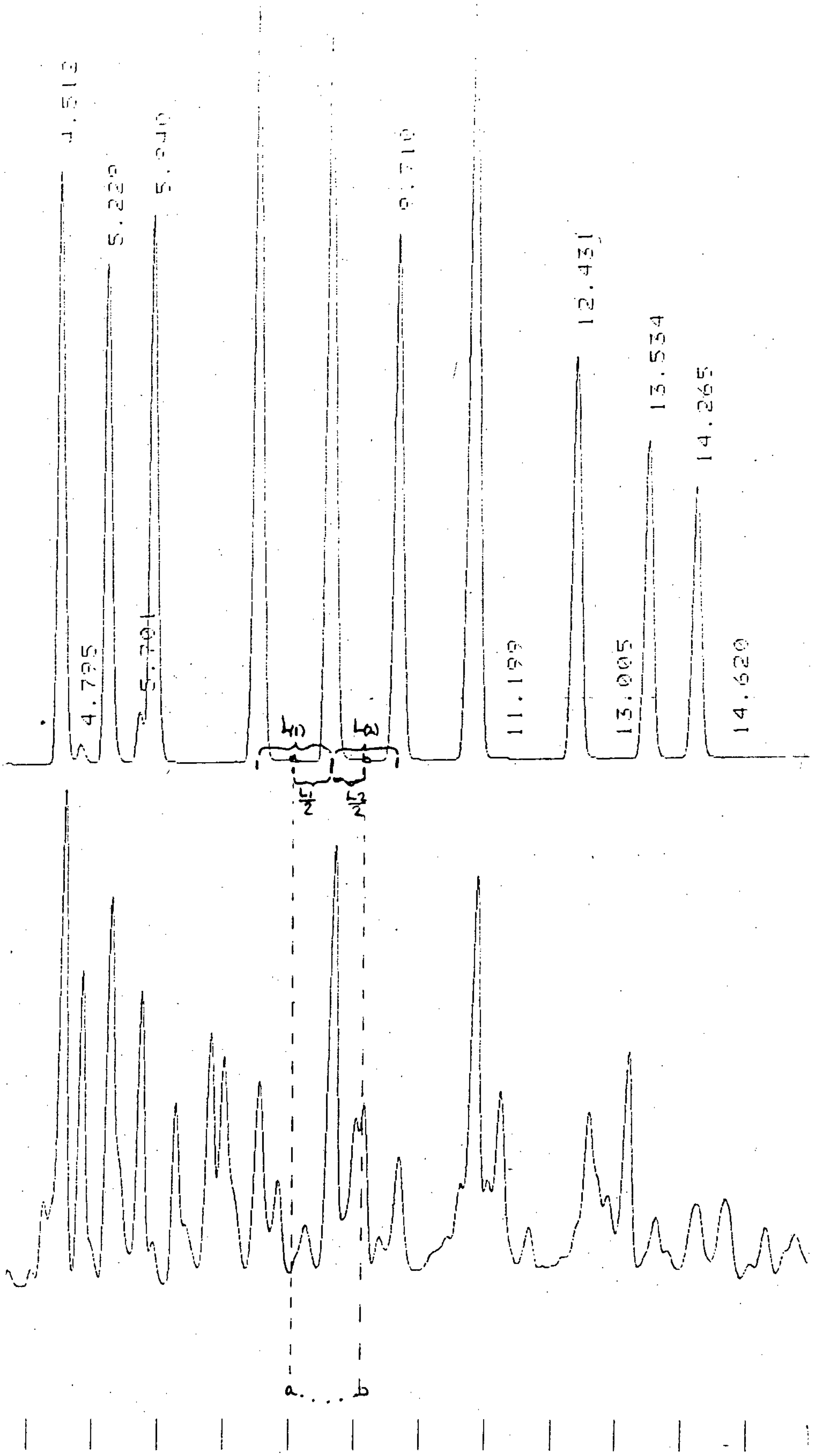
c) Courbe de distribution du point d'ébullition:

1°) Délimitation du domaine de chaque RRF, selon le chromatogramme de calibration, comme dans l'exemple à la page suivante.

2°) Vol. (a, b) = Aire (a, b) x RRF (a, b)

3°) Tabulation du rapport du volume ainsi obtenu sur le volume total versus les Temps de rétention correspondant à la fin des intervalles mentionnés à la figure 2.



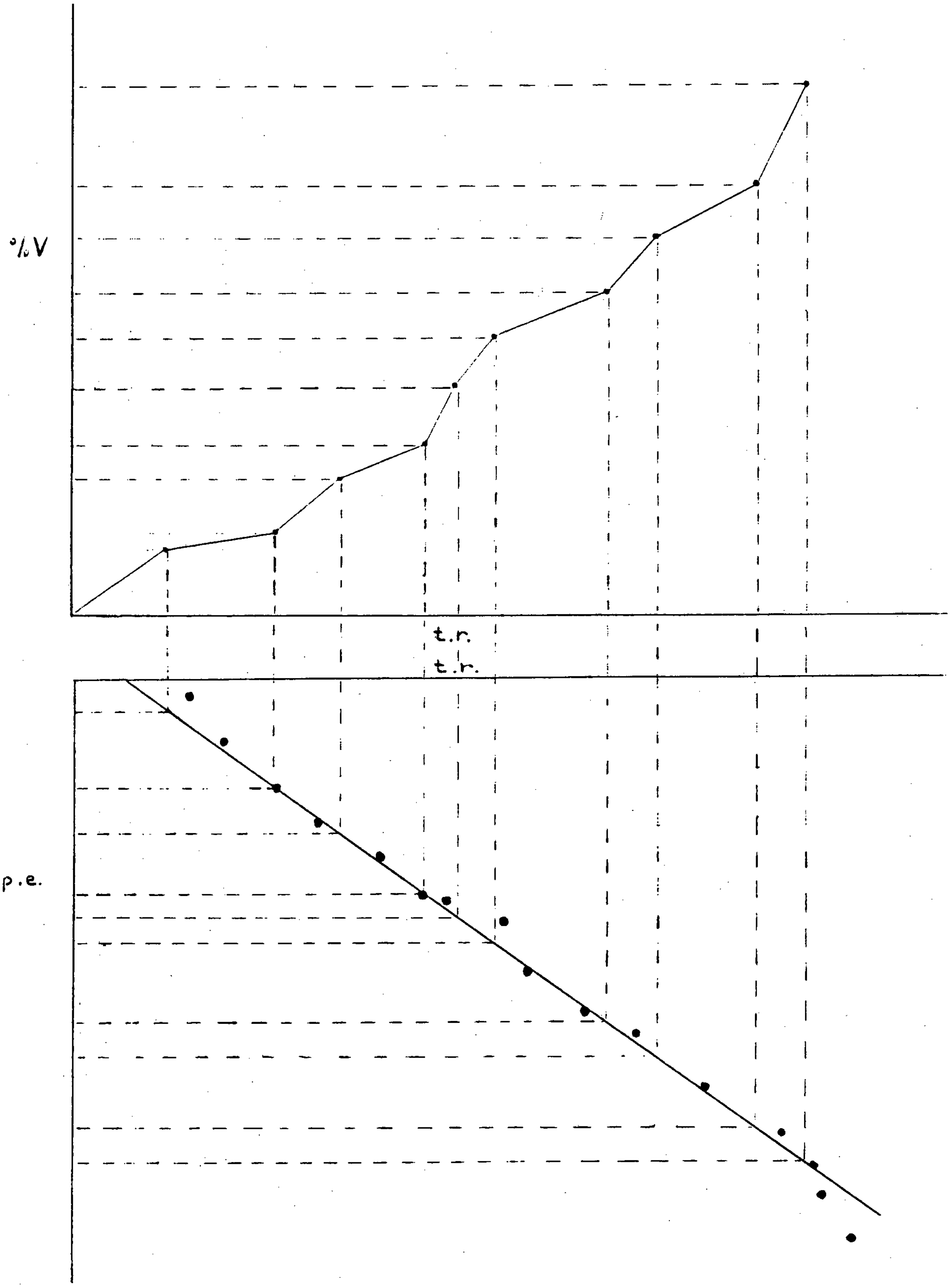


Ainsi, RRFx devient le multiplicateur de toute l'aire entre les points a, b.

4^0) Identification dans l'échantillon des pics de $n-C_3$, $i-C_4$ et $n-C_4$ par comparaison avec les Temps de calibration, et détermination des %(volume) de ces composants.

5^0) Détermination du Temps de rétention associé à chaque x%(volume), de 0,5% à 99,5% (0,5% = point d'ébullition initial, 99,5% = point d'ébullition final), à l'aide d'une extrapolation linéaire entre chaque point et le suivant.

6⁰) Détermination de la température (⁰C ou ⁰F) associée à chaque x%(volume), à l'aide de la courbe du point d'ébullition versus le Temps de rétention:



Addendum: Pour calculs de la pression de vapeur Reid et de la corrélation D-86, voir document ASTM D-3710 en annexe.

IV Notes sur les réglages du chromatographe (CC)

Colonnes: SE-30 5% G.AW DMCS
mesh: 60/80
dimensions: 5' x .125" (dia. ext.)

Gaz porteur: helium (He)
débit: 30ml/min

Volume d'injection: 1ml
* Si on change ce volume, il faut recalculer les RRF, car ils fluctuent avec les variations de volume.

Usage du auto-zéro: Son usage est indiqué dans les périodes de stabilisation entre les analyses, pour actualiser la ligne de base.

Détecteur:

Type: TCD (stabilisation: 24 hres après installation)
Range: .5
Atténuation: 64

Programmation de

Température: -20^0C à 190^0C
Taux d'accroissement: 9 C/min.
Temps: 23,33 min.

Températures:

injecteurs: 220^0C
TCD : four: 270^0C
filament: 290^0C

V Résolution

Les conditions d'opération du GC doivent être choisies de façon à pouvoir séparer correctement tous les composants du standard de calibration de la méthode D-3710. Le système doit ainsi pouvoir distinguer le début et la fin des premiers pics éluant de la colonne (n-C_3 et suivants), mais de façon à éviter l'évasement excessif des derniers pics.

On peut évaluer cette résolution de la façon suivante:

$$R = 2D/(Y_1 \quad Y_2)$$

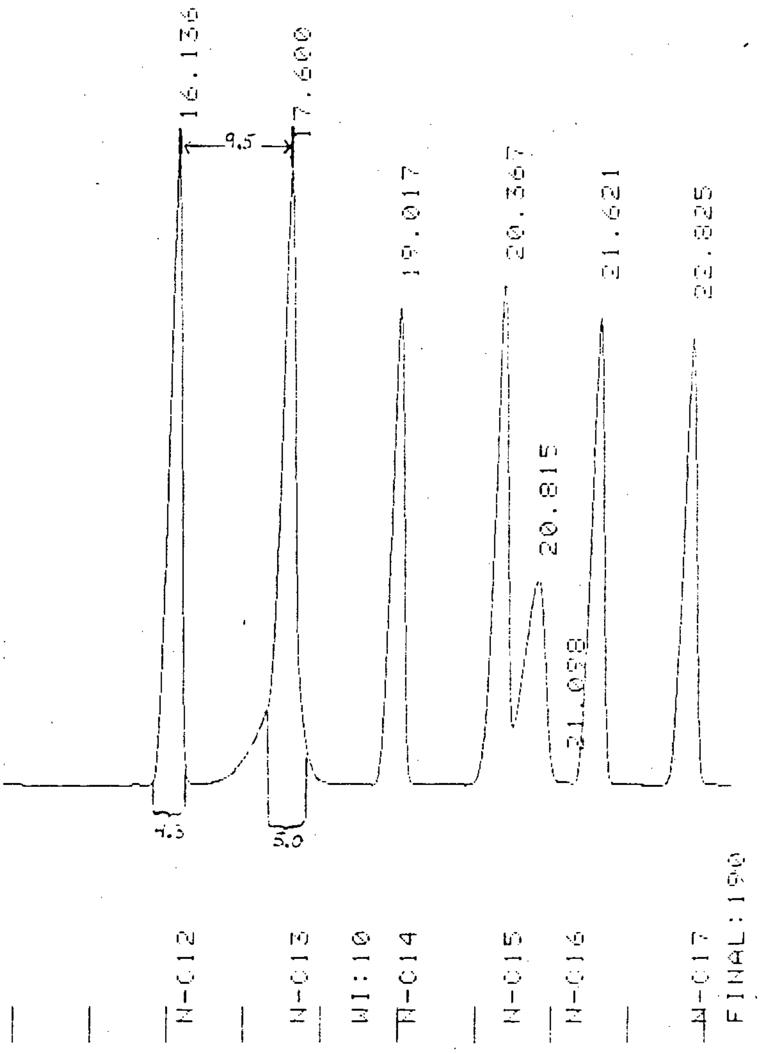
R doit se situer entre 2 et 4

$R = 2D/Y_1 + Y_2$

$R = 29,5/(4,3 + 5,0)$

$R = 19,0/9,3$

$R = 2,04$



CONCLUSION

Il est, avant tout, essentiel de préciser qu'une nouvelle calibration (calcul des RRF's) doit être effectuée si la dernière en date remonte à plus de quatre semaines, car un séjour aussi prolongé de la colonne dans l'appareil, même à température ambiante, occasionne une altération non négligeable de la phase liquide.

Aussi, une nouvelle ligne de base doit être établie à chaque jour d'utilisation, la réponse du détecteur variant selon le taux d'émanations gazeuses de la colonne.

La méthode décrite dans ces pages offre, lorsque bien rodée, une bonne reproductibilité. Il est clair que les principales sources d'écarts relatifs aux valeurs attendues sont redevables à l'encrassement ou au réglage inadéquat du détecteur.

La corrélation D-86 de la méthode se rapproche raisonnablement des valeurs expérimentales. On ne peut attendre beaucoup de cette corrélation, les manipulations inhérentes à chaque méthode étant très différentes. Il faudra sans doute, pour une ultime évaluation de la validité de la méthode D-3710, attendre les résultats d'un éventuel programme d'échanges portant sur ladite méthode.

Denis Boudreau
26 mars 1984

AMERICAN NATIONAL STANDARD ANSI/ASTM D 3710 - 78'

Standard Test Method for
BOILING RANGE DISTRIBUTION OF GASOLINE AND GASOLINE FRACTIONS BY GAS CHROMATOGRAPHY[1]

This standard is issued under the fixed designation D 3710; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

NOTE—Section 11.2.1 was editorially changed in March 1980.

1. Scope

1.1 This method covers determination of the boiling range distribution of gasoline and gasoline components. The method is applicable to petroleum products and fractions with a final boiling point of 260°C (500°F) (Note 1) or lower as measured by this method.

NOTE 1—The values stated in U.S. customary units are to be regarded as standard. The values stated in SI units are for information only.

1.2 The method is designed to measure the entire boiling range of gasoline and gasoline components with either high or low Reid vapor pressure and is commonly referred to as gas chromatography (GC) distillation (GCD).

2. Applicable Documents

2.1 *ASTM Standards:*

D 86 Distillation of Petroleum Products[2]

D 323 Test for Vapor Pressure of Petroleum Products (Reid Method)[2]

D 1265 Sampling Liquefied Petroleum (LP) Gases[2]

3. Summary of Method

3.1 The sample is introduced into a gas chromatographic column which separates hydrocarbons in order of boiling point. Conditions are selected so as to measure isopentane and lighter saturates discretely. Normal pentane and heavier compounds are not completely resolved but are measured as pseudo components of narrow boiling range. The column temperature is raised at a reproducible rate and the area under the chromatogram is recorded throughout the run. Boiling temperatures are assigned to the time axis from a calibration curve, obtained under the same conditions by running a known mixture of hydrocarbons covering the boiling range expected in the sample. From these data the boiling range distribution of the sample is obtained.

4. Significance and Use

4.1 The determination of the boiling range distribution of gasoline by GC distillation provides an insight into the composition of the components from which the gasoline has been blended. This insight also provides essential data necessary to calculate the vapor pressure of gasoline, which has been traditionally determined by Method D 323. In addition, the Method D 86 distillation curve can be predicted using GCD data.

4.2 The GCD method facilitates on-line controls at the refinery, and its results offer improved means of describing several car performance parameters. These parameters include: (*1*) car-starting index, (*2*) vapor-lock index or vapor-liquid ratio, and (*3*) warm-up index. The car-starting and vapor-lock indexes have been found to be mostly affected by the front end of the Method D 86 distillation curve (up to about 200°F (93°C)). The warm-up index is affected by the middle and to a lesser extent by the back end of the Method D 86 curve, that is, the temperatures corresponding to the 50 to 90 % off range. Since the boiling range distribution provides

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[1] This method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants.

Current edition approved Aug. 25, 1978. Published October 1978.

[2] *Annual Book of ASTM Standards*, Part 23.

fundamental information on composition, an improved expression for the above performance parameters may be worked out, even when the boiling range distribution curve is not smooth. Currently, car performance cannot be assessed accurately under such conditions.

5. Definitions

5.1 *response factor*—a constant of proportionality that converts area to liquid volume.

5.2 *volume count*—the product of the area under a peak and a response factor.

5.3 *initial boiling point* (IBP)—the point at which a cumulative volume count equal to 0.5 % of the total volume count under the chromatogram is obtained.

5.4 *final boiling point* (FBP)—the point at which a cumulative volume count equal to 99.5 % of the total volume count under the chromatogram is obtained.

5.5 *relative molar response*—the measured area of a compound divided by the moles present in the synthetic mixture relative to an arbitrarily chosen component.

5.6 *system noise*—the difference between the maximum and minimum area readings per second for the first 20 area readings in the blank run.

6. Apparatus

6.1 *Chromatograph*—Any gas chromatograph may be used that meets the performance requirements in Section 8. Place in service in accordance with manufacturer's instructions. Typical operating conditions are shown in Table 1.

6.1.1 *Detector*—The method is restricted to the use of the thermal conductivity dectector. This restriction will be removed if further cooperative testing indicates the suitability of the flame ionization detector also. Detector stability must be such that the sensitivity and baseline drift requirements as defined in Section 8 are met. The detector also must be capable of operating continuously at a temperature equivalent to the maximum column temperature employed, and it must be connected to the column so as to avoid any cold spots.

NOTE 2—Care must be taken that the sample size chosen does not allow some peaks to exceed the linear range of the detector. With thermal conductivity detectors, sample sizes of the order of 1 to 5 μl generally are satisfactory.

NOTE 3—It is not desirable to operate the detector at temperatures much higher than the maximum column temperature employed. Operation at higher temperatures only serves to shorten the useful life of the detector, and generally contributes to higher noise levels and greater drift.

6.1.2 *Column Temperature Programmer*—The chromatograph must be capable of program temperature operation over a range sufficient to establish a retention time of at least 15 s for propane and of allowing elution of the entire sample within a reasonable time period. Subambient capability may be required. The programming rate must be sufficient reproducible to meet the requirements of 8.7.

NOTE 4—If the column is operated at subambient temperature, excessively low initial column temperature must be avoided, to ensure that the stationary phase remains liquid. The initial temperature of the column should be only low enough to obtain a calibration curve meeting the specifications of the method.

6.1.3 *Sample Inlet System*—The sample inlet system must be capable of operating continuously at a temperature equivalent to the maximum column temperature employed, or provide on-column injection with some means of programming the entire column, including point of sample introduction up to the maximum temperature required. The sample inlet system must be connected to the chromatographic column so as to avoid any cold spots.

6.1.4 *Flow Controllers*—Chromatographs must be equipped with constant-flow controllers capable of holding carrier gas flow constant to ±1 % over the full operating temperature range.

6.2 *Sample Introduction*—Sample introduction may be either by means of a constant-volume liquid sample valve or by injection with a microsyringe through a septum. If the sample is injected manually, cool the syringe to 0 to 4°C (32 to 40°F) before taking the sample from the sample vial.

NOTE 5—Automatic liquid-sampling devices or other sampling means, such as sealed septum-capped vials, may be used, provided no loss of light ends occurs. The system must be operated at a temperature sufficiently high to vaporize completely hydrocarbons with an atmospheric boiling point of 260°C (500°F), and the sampling system must be connected to the chromatographic column so as to avoid any cold spots.

6.3 *Recorder* — A recording potentiometer with a full-scale response time of 2 s or less may be used.

6.4 *Column* — Any column and conditions may be used, provided, under the conditions of the test, separations are in order of boiling points and the column meets the performance requirements in Section 9. See Table 1 for columns and conditions that have been used successfully. Since a stable baseline is an essential requirement of this method, matching dual columns are required to compensate for column bleed, which cannot be eliminated completely by conditioning alone.

6.4.1 *Column Preparation* — Any satisfactory method, used in the practice of the art, that will produce a column meeting the requirements of Section 9, may be used. The column must be conditioned at the maximum operating temperature to reduce baseline shifts due to bleeding of column substrate.

NOTE 6 — The column may be conditioned very rapidly and effectively by the following procedure:

(*1*) Disconnect column from detector.

(*2*) Purge the column thoroughly at ambient temperature with carrier gas.

(*3*) Turn off the carrier gas and allow the column to depressurize completely.

(*4*) Raise the column temperature to the maximum operating temperature and hold at this temperature for at least 1 h with no flow through the column.

(*5*) Cool the column to at least 100°C before turning on carrier gas again.

(*6*) Program the column temperature up to the maximum several times with normal carrier gas flow. The column then should be ready for use.

NOTE 7 — An alternative method of column conditioning, which has been found effective for columns with an initial loading of 10 % liquid phase, consists of purging the column with carrier gas at the normal flow rate while holding the column at maximum operating temperature for 12 to 16 h.

6.5 *Integrator* — Means must be provided for determining the accumulated area under the chromatogram. This can be done by means of a computer, or automatic operation can be achieved with electronic integration. A timing device is used to record the accumulated area at set time intervals. The same basis for measuring time must be used to determine retention times in the calibration, the blank, and the sample. If an electronic integrator is used, the maximum area measurement must be within the linear range of the integrator.

6.6 *Sample Containers* — Pressure cylinders or vials with septums should be provided for the calibration mixture and samples to avoid loss of light ends.

6.7 *System* — Any satisfactory combination of the above components that will meet the performance requirements of Section 9.

7. Reagents and Materials

7.1 *Calibration Mixture* — A synthetic mixture of pure liquid hydrocarbons of known boiling point covering the boiling range of the sample. At least one compound in the mixture must have a boiling point equal to or lower than the initial boiling point of the sample, and one compound must have a retention time greater than any component in the sample. The concentration of all compounds heavier than *n*-butane must be known within 0.1 %. The synthetic composition shown in Table 2 should be used for gasoline analysis. Compounds necessary for evaluation of system performance are noted in Table 2.

NOTE 8 — If the sample contains significant quantities of compounds that can be identified on the chromatogram, these peaks may be used as internal boiling point calibrations.

NOTE 9 — Two calibration mixtures may be used for convenience. One that would contain known concentrations of isopentane and heavier compounds would be used for determining response factors, sensitivity, and concentration repeatability. The other would contain a complete boiling range of compounds including propane, butane, and isobutane, whose concentrations are known only approximately. It would be used for measuring resolution, skewness, retention time repeatability, polarity, and retention time-boiling point relationship.

NOTE 10 — If the sample is known to contain more than 5 % benzene, dimethyl pentane should be replaced by benzene in the calibration mixture.

7.2 *Carrier Gas* — Helium or hydrogen for use with thermal conductivity detectors.

7.3 *Liquid Phase for Columns:*

NOTE 11 — The following materials have been used successfully as liquid phases:

Silicone gum rubber GE-SE-30[3]
Silicone gum rubber OV-1[4]
Silicone gum rubber OV-101[4]
Silicone gum rubber Supelco 2100[5]
Silicone gum rubber UC-W98[6]

7.4 *Solid Support* — Usually crushed fire brick or inert diatomaceous earth such as Chromosorb P, G, or W,[7] acid-washed, di-

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[3] Registered trademark of General Electric Co.

[4] Registered trademark of Ohio Valley Specialty Chemical Co.

[5] Registered trademark of Supelco, Inc.

[6] Registered trademark of Union Carbide Co.

[7] Registered tradmark of Johns-Manville Co.

methyl silanized. Sieve size and support loading should be such that it will give optimum resolution and analysis time. In general, support loadings of 3 to 10 % have been found most satisfactory but higher ones have been used as shown in Table 1.

8. Safety Precautions

8.1 Benzene is a toxic substance. Avoid direct contact with the skin and inhalation of its vapors. Work with benzene in a fume hood where possible.

8.2 Full-range gasolines are highly flammable. Bring only small amounts in tightly sealed containers into the laboratory. Keep gasoline vapors away from sources of ignition such as open flames and electric sparks.

8.3 Hydrogen is a highly flammable gas. If it is used, take special care to eliminate any leaks in the equipment. Avoid venting, but if the gas is vented, vent it only into an exhaust system with no sources of ignition.

9. System Performance

9.1 *Resolution*—For samples containing isopentane and lighter materials, the system must be able to identify the beginning and end of isopentane and lighter saturated compounds as they elute from the column. Individual peaks must be resolved from adjacent peaks so that the height at the valley above the baseline is not more than 5 % of the height of the smaller peak adjacent to it. The resolution, R, between nC_{12} and nC_{13} must be between 2 and 4 when calculated in accordance with the following equation as shown in Fig. 1:

$$R = 2D/Y_1 + Y_2$$

where:

D = time in seconds between nC_{12} and nC_{13} apexes,

Y_1 = peak width of nC_{12} in seconds, and

Y_2 = peak width of nC_{13} in seconds.

9.2 *Sensitivity and Noise*—These criteria test the sensitivity and noise of the total system. From the first 20 readings or time intervals of the blank run, calculate the noise as the difference between the maximum area reading per second minus the minimum reading per second. From the measurements on the calibration mixture, calculate the signal/noise ratio, $A/(n \times s)$, were A = total area of the hexane peak, N = noise, and S = width of the hexane peak in seconds. This value must not be less than 10 for each 0.05 volume percent of hexane in the calibration mixture, for example, 200 for 1 %. If the noise is undetectable, assume the noise to be 1 count per second.

9.3 *Drift*—From the blank run, calculate by the following method, a total area measured after the start of the run until the end of the run. Adjust the apparatus so that all measurements can be read whether positive or negative. On some equipment such as integrators, readings will need to be positive and increasing in value. Obtain the absolute difference between the average area reading in the first five time intervals and the individual readings in each time interval from the start of the blank run until the end. Sum these differences to obtain the total area for the blank. The total area measurement from the blank run must not be greater than 2.0 % of the total area measurement of the calibration mixture.

9.4 *Skewing of Peaks*—Calculate the ratio A/B on peaks in the calibration mixture as shown on Fig. 2. A is the width in seconds of the part of the peak ahead of the time of the apex at 5 % of peak height, and B equals the width in seconds of the part of the peak after the time of the apex at 5 % of peak height. This ratio must not be less than 0.5 nor more than 2.0.

NOTE 12—A ratio of more than 2.0 is probably due to overloading of the column. This may be corrected by smaller sample size, higher loading of the liquid phase on the packing, or larger diameter column. A ratio of less than 0.5 probably indicates tailing, overloading the detector, or loss of liquid substrate. The column must be changed when tailing becomes excessive. It is possible that the peak shape may be distorted due to a combination of these reasons.

9.5 *Retention Time*—The system must be sufficiently repeatable when testing the calibration mixture to obtain peak maxima retention time repeatability (maximum difference between duplicate results) of 3 s for isopentane and lighter compounds, if present. The maximum difference between duplicate results of retention times of the normal pentane and heavier compounds must not be greater than a time equivalent to 2°C (3°F). In addition, the retention time of the apex of the first peak in the calibration mixture should be at least 15 s.

9.6 *Polarity*—Calculate the boiling point retention time relationship specified in 11.2.2, using only the *n*-paraffins. Using the observed retention time of the aromatic compounds, calculate their apparent boiling points. Compare the apparent boiling points of the aromatics with their known boiling points. The apparent boiling point of the aromatic compounds must not deviate more than 6°C (10°F) from linearity or normal paraffins in the calibration mixture.

9.7 *Area Measurement*—The area measurement may be made by an electronic integrator or an analog-to-digital converter in conjunction with a computer. As the run progresses, the amount of material eluted from the column is measured from time zero in time "slice" areas or counts at specified time intervals. The counts are summed continuously, and the time intervals are equated to equivalent temperatures using the calibration curve generated in 11.2.2. Continue measurement for 2 min after the apex of the last peak or until the chromatogram returns to a constant baseline at the end of the run. Duplicate results on consecutive runs on the area percent of the compounds in the calibration mixture must not differ by more than 0.1 %.

9.7.1 Time intervals need not be uniform throughout the run. However, it is important that all measurement be on the same basis for the blank, calibration, and sample. No interval shall be greater than 0.5 % of the total length of the run. In addition, in order to facilitate the measurement of light ends, the size of the time intervals for the isopentane and lighter compounds should be small enough to allow measurement of their areas and times to peak maxima.

NOTE 13—The end of the run may be defined by using the following algorithm: find the time where the rate of change of the chromatographic signal is less than or equal to a specified value (0.05 mV/min and 0.001 % of the total area under the chromatogram have been used successfully). Then search for 1 min before and after that time. The point where the number of counts per slice is at a minimum in that 2 min period is defined as the end of the run.

9.8 *Difference from Calibration Mixture*—Multiply the area of each peak in the calibration mixture by the liquid volume response factor calculated in 12.2, and normalize the volume percent of each compound so that the volumes of all compounds heavier than *n*-butane add up to 100.0. Compare the volume percent of each compound heavier than *n*-butane with the known percent. The difference between the calculated and known percentages must not be greater than 0.5.

10. Sampling

10.1 *Sampling from Bulk Storage:*

10.1.1 *Cylinder*—Refer to Method D 1265 for instructions on introducing samples into a cylinder from bulk storage. The cylinder should be pressurized with carrier gas to a pressure of at least 345 kPa (50 psi) above the vapor pressure of the sample. If the sample is to be transferred to another vessel such as a vial with septum, the cylinder must be cooled to a temperature between 0 and 4°C (32 and 40°F).

10.1.2 *Open Containers*—Refer to Method D 270 for instructions on introducing samples into open-type containers from bulk storage. Cool the container and its contents to 0 to 4°C (32 to 40°F) before removing any sample from it.

10.2 *Sampling from Open-Type Containers*—Follow the instructions in Method D 323 for transferring material from an open-type container.

11. Procedure

11.1 *Blank*—After conditions have been set to meet performance requirements, program the column temperature upward to the maximum temperature to be used. Following a rigorously standardized schedule, cool the column to the selected starting temperature. At the exact time set by the schedule, without injecting a sample, start the column temperature program. Measure and record the area in each time interval from the start of the run until the end of the run as specified in 9.7. Make a blank run at least daily.

11.1.1 In order for the blank run to be valid, it must meet the drift requirement specified in 9.3. In addition, no peaks must be found such that the difference in area readings per second in consecutive time intervals be greater than five times the noise. If the noise is not detectable, assume it to be 1 count per second.

NOTE 14—The identification of a constant baseline at the end of the run is critical to the method. Constant attention must be given to all factors that influence baseline stability, such as substrate bleed.

11.2 *Calibration:*

11.2.1 Using the same conditions described in 11.1, inject the calibration mixture into the chromatograph. Record the data in such a manner that retention time of peak maxima and peak area of the individual components are obtained. As noted in 9.7, this can be done by means of a computer or integrator.

NOTE 15—When determination of peak maxima and peak area is done by the time slice technique, the following algorithms may be used to verify the start of peak, end of peak, and peak maxima: A peak is defined as starting in that time slice in which the rate of change of the chromatographic signal is greater than a specified value (0.05 mV/min and 0.001 %/s have been used successfully). This criterion must be confirmed for two consecutive time segments in order to be valid. Once a peak is detected, the end is determined by one of two criteria. The first applies when there is good resolution between peaks. The peak may be defined as ending when the rate of change of the chromatographic signal is less than the value specified above. The second criterion applies when resolution between peaks is not complete. The first peak ends when, after the apex has passed, the area per time segment reaches a minimum and starts to increase. The retention time of peak maxima may be determined by the following equation, as shown in Fig. 3:

$$t_{\max} = t_i + (t_{i+1} - t_i)\, A_{i+1}/(A_{i-1} + A_{i+1})$$

where:

$t_{\max}$ = retention time of peak maxima,
t_i = time to start of segment i,
t_{i+1} = time to start of segment $i + 1$,
A_{i+1} = area of segment that starts at t_{i+1}, and
A_{i-1} = area of segment that starts at t_{i-1}.

For systems in which the output is in units other than millivolts, an equivalent measure of the slope may be used.

11.2.2 Plot the retention time of the maxima of each peak versus the corresponding normal boiling point in degrees Celsius (or Fahrenheit) as shown in Fig. 4. If the sample is known to contain less than 5.0 % aromatics, do not include aromatic compounds in the retention time calibration curve.

NOTE 16—For best precision, the calibration curve should be essentially a linear plot of boiling point versus retention time. In general, the lower the initial boiling point of the sample, the lower will be the starting temperature of the chromatographic column. If the starting temperature is too high, there will be considerable curvature at the lower end of the curve, and loss of precision in that boiling range. Since it is impractical to operate the column so as to eliminate curvature completely at the lower end of the curve where initial boiling points below ambient temperature are encountered, at least one point on the curve should have a boiling point lower than or equal to the initial boiling point of the sample. Extrapolation of the curve at the upper end is more accurate, but for best accuracy, calibration points should bracket the boiling range of the sample at both the low and high ends.

11.2.3 The boiling point retention time calibration curve must be checked at least daily by either the calibration mixture or a secondary standard of known boiling point characteristics.

NOTE 17—If peaks in the sample are used as boiling point calibration marks, the calibration mixture need not be run. However, it may prove helpful in establishing identity of peaks in the sample to run the calibration mixture once. Furthermore, precision may be improved in some cases by adding to the sample an *n*-paraffin, selected so as to be resolved completely from the sample, to serve as an additional boiling point calibration. Plot the retention times of the peaks versus the corresponding atmospheric boiling points to obtain the calibration curve.

11.3 *Sampling:*

11.3.1 Using the exact conditions and time basis as were used in the blank and calibration, inject the sample into the chromatograph. Disregarding peaks (if any) before propane, measure and record the area of each time segment at time intervals as specified in 9.7.

12. Calculations

12.1 *Drift Correction*—Drift correction is not necessary if the drift is less than 0.5 % as calculated in 9.3.

12.1.1 Correct the blank, calibration, and sample runs for initial offset from zero by subtracting from each time interval the average area of the first five time intervals in the corresponding run. Omit from the average any readings (extraneous peaks) that are more than three times the noise as defined in 9.2.

12.1.2 Correct the calibration and sample for drift by subtracting the corrected area of each time segment of the blank from the corresponding segment of the sample.

NOTE 18—The corrected area for each time segment is calculated as follows:

$$A_{Ci} = A_i - A_{Bi} - (O - O_B)$$

where:

A_{Ci} = corrected area of segment i, sample or calibration,
A_i = uncorrected area of segment i,
A_{Bi} = area of corresponding segment of blank,
O = offset from run, sample or calibration, and
O_B = offset from blank.

12.1.3 An alternative method of correcting for drift and offset is by subtracting a triangular segment of area based on the sample itself as illustrated in Fig. 5.

NOTE 19—For the scheme shown in Fig. 5, the corrected area for each time segment is calculated as follows:

$$A_{Ci} = A_i - \left[A_o + (A_f - A_o)\left(\frac{t_i - t_o}{t_f - t_o}\right)\right]$$

where:

A_{Ci} = corrected area of segment i, sample or calibration,
A_i = uncorrected area of segment i,
A_o = average area of last five segments before start of first peak,
A_f = area of first segment after end of last peak,
t_i = time to segment i from beginning of run,
t_o = time to last segment before start of first peak, and
t_f = time to first segment after end of last peak.

12.1.4 In cases where the calibration is peak-integrated instead of time-sliced, the drift corrections need not be applied.

12.2 *Response Factors:*

12.2.1 Using the corrected areas from the calibration run and composition of the calibration mixture, calculate the response factor relative to the factor for nC_7 for all compounds iC_5 and heavier:

$$\text{Response factor, } F_i = (V_i \times A_{c_o})/(V_o \times A_{c_i})$$

where:

F_i = response factor of the compound,
A_{c_i} = corrected area for each pure compound,
V_i = volume percent from the calibration mixture,
A_{c_o} = corrected area of nC_7, and
V_o = volume percent of nC_7 in the calibration mixture.

12.2.2 Determine the response factors for propane, isobutane, and n-butane in the following manner. Calculate the relative molar response, RMR, for each of the normal paraffins starting with nC_5 as follows:

$$\text{RMR}_i = (A_{c_i} \times m_o)/(A_{c_o} \times m_i)$$

where:

RMR_i = relative molar response for the compound,
m_i = mole percent of the compound in the calibration mixture, and
m_o = mole percent of nC_7 in the calibration mixture.

The RMR is a linear function of molecular weight.[8] The measured RMR's are fit to the linear equation RMR = a $MW + b$ employing the least squares technique. The RMR for propane and n-butane is calculated using the resulting equation. For isobutane, use the RMR measured for n-butane. Calculate response factors for these three components as follows:

$$\text{Response factor, } F_i = (\text{MW}_i \times \text{RMR}_o \times \text{Den}_o)/(\text{MW}_o \times \text{RMR}_i \times \text{Den}_i)$$

where:

MW_i = molecular weight of the compound,
MW_o = molecular weight of nC_7,
RMR_i = relative molar response of the compound,
RMR_o = relative molar response of nC_7,
Den_i = relative density of the compound, and
Den_o = relative density of nC_7.

Typical response factors along with relative densities are shown in Table 2.

NOTE 20—If the concentrations of propane and butane in the calibration mixture are known, differences noted between the observed and calculated response factors indicate loss of front-end components. If a fresh calibration mixture is used, these differences could be indicative of sampling problems. Deviation of the response factors of the heavier components from the straight-line relationship could indicate problems in volatilizing the sample. Possible reasons include injection port temperature being too low, insufficient carrier gas flow, or lack of homogeneity in sampling. Figure 6 illustrates these effects.

12.2.3 Apply the response factor for each compound in the calibration mixture to the

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[8] Messner, A. E., et al, "Correlation of Thermal Conductivity Cell Response with Molecular Weight and Structure," *Analytical Chemistry*, ANCHA, Vol 31, No. 2, February 1959, pp. 230–233.

corrected areas of all time intervals in the sample that fall between a point (*a*) that is halfway between the observed apex of that compound and the observed apex of that compound and the observed apex of the preceding compound, and a point (*b*) that is halfway between the observed apex of that compound and the observed apex of the succeeding compound. The response factors used may differ according to sample type. For commercial gasolines, typical response factors are shown in Table 2. For gasoline blending components containing small amounts of aromatics, such as alkylates, the aromatic response factors should be omitted and only paraffin response factors used. The response factors measured may be used until such time as the detectors or columns are changed or there is some reason to suspect that their values are no longer applicable.

12.3 *Calculation of Sample:*

12.3.1 For each time segment between the beginning of the first peak and the end of the last peak, multiply the area by the suitable response factor to get volume counts. Divide the cumulative volume counts at the end of each interval by the total volume counts and multiply by 100. This will give the cumulative percent of sample recovered at each interval.

12.3.2 Tabulate the cumulative volume percent recovered at each interval and the retention time at the end of the interval. Using linear interpolation where necessary, determine the retention time associated with 0.5 and 99.5 volume % recovered. These are respectively the initial and final boiling points. Determine the retention time for each volume percent off between 1 and 99.

12.3.3 For each volume percent and its associated retention time, determine the corresponding temperature from the calibration curve (11.2.2). Use linear interpolation between all calibration points.

12.3.4 Identify individually the propane through isopentane peaks by comparing the retention time of each peak to the corresponding retention time in the calibration run. Check to see that the retention time of the apex of the propane, iso-, and normal butane and isopentane peaks is within a time equivalent to 3°C (5°F) of the calibration run. Note any isopentane or lighter component that is apparently absent. Calculate the volume percent of the individual compounds by using the suitable response factors. Include any peaks between normal butane and isopentane with the normal butane peak.

13. Report

13.1 Report the temperature to the nearest 0.5°C (1°F) at 1 % intervals between 1 and 99 %, and at 0.5 % and 99.5 %. The report format is shown in Table 3. Other formats based on users' needs may also be employed.

13.2 Report volume percent of isopentane and lighter compounds individually. This provides a more absolute basis for describing commercial gasolines than the IBP.

NOTE 21 – Some olefins will be measured with butane and isopentane. See 12.3.4.

14. Precision

14.1 The precision of this method depends on the shape of the boiling range distribution curve. Both repeatability and reproducibility vary with the slope of the curve, $dT/d\%$ where T = temperature and % = percent off. If the value of the slope is small, the temperature corresponding to a given percent off will be determined very precisely. For example, if a gasoline sample contains 10 % toluene and this toluene elutes from the column between 55 and 65 %, the 60 % cutpoint will vary by no more than 0.6°C (1°F) between laboratories.

14.2 If the slope is large, as it is at some sections of the boiling range distribution curve, standard deviations for single samples between laboratories can be as high as 8°C (15°F). This may occur for gasolines containing large concentrations of individual compounds. For gasolines with no compounds present in concentrations above 10 %, this value would be lower. At the extreme back end of the curve, the slope becomes very large and larger differences between laboratories can be expected.

14.3 The following criteria should be used for judging acceptability of results (95 % confidence). These data were generated from analyses of commercial gasolines with a wide range of volatilities. Caution should be exercised when applying these criteria and reference should be made to the actual boiling range distribution curve.

14.3.1 *Repeatability*—The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only 1 case in 20:

Percent Recovered	Repeatability
0.5 (IBP)	1.0°C (2°F)
1 to 25	1.0°C (2°F)
26 to 75	1.0°C (2°F)
76 to 99	1.0°C (2°F)
99.5 (FBP)	1.0°C (2°F)
Concentration	
C_3	6 % (relative)
isoC_4	2 % (relative)
nC_4	2 % (relative)
isoC_5	2 % (relative)

14.3.2 *Reproducibility*—The difference between two single and independent results, obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only 1 case in 20:

Percent Recovered	Reproducibility
0.5 (IBP)	4.5°C (8°F)
1 to 25	4.5°C (8°F)
26 to 75	6.0°C (11°F)
76 to 99	9.0°C (16°F)
99.5 (FBP)	12.0°C (22°F)
Concentration	
C_3	70 % (relative)
isoC_4	29 % (relative)
nC_4	14 % (relative)
isoC_5	6 % (relative)

TABLE 1 Gas Chromatography Column and Conditions

Column:					
Liquid phase, material	UCW-982	Supelco 2100	UCW-98	OV-101	UCW-98
weight %	10	20	10	10	10
Solid support, material	Chromosorb P	Chromosorb W	Chromosorb G	Chromosorb P	Supelcoport
mesh size	80/100	80/100	60/80	60/80	80/100
Length, m (ft)	0.5 (1.5)	1.5 (5)	0.9 (3)	1.2 (4)	1.5 (5)
Outside diameter, mm (in.)	6.4 (1/4)	3.2 (1/5)	6.4 (1/4)	3.2 (1/8)	3.2 (1/8)
Temperatures:					
Initial column temperature, °C	−30	40	−20	0	0
Final column temperature, °C	250	250	200	250	230
Detector temperature, °C	250	250	345	250	250
Injection zone temperature, °C	250	300	345	250	230
Operating Variables:					
Program rate, °C/min	10.6	16	10	15	16
Carrier gas	He	He	He	He	He
flow rate, cm^3/min	50	30	60	29	30
Sample size, µl	3	2	3	2	1
Detector voltage (or mA)	150 mA	160 mA	135 mA	. . .	175 mA
Instrument:					
Detector type	TC	TC	TC	TC	TC
Sampling system	automatic syringe	syringe	syringe	valve	valve
Area measurement method	integrating A/D	integrating A/D	integrating A/D	time slice	time slice
Time slices per second	2	1/2	5	5	1/2

TABLE 2 Calibration Mixture

Peak Number	Compound Identification	NBP, °F	Relative density,[A] 60/60°F	Approximate Volume, %	Typical Thermal Conductivity Response Factors
1[B]	nC_3	−44	0.5077	1	1.15
2[B]	$isoC_4$	11	0.5631	3	1.14
3[B]	nC_4	31	0.5844	10	1.07
4[B]	$isoC_5$	82	0.6248	9	1.08
5	nC_5	97	0.6312	7	1.03
6	2-MeC_5	140	0.6579	5	1.03
7[C]	nC_6	156	0.6640	5	1.01
8[D]	2,4-DiMeC_5	177	0.6772	5	1.07
9	nC_7	209	0.6882	9	1.00
10[C]	Toluene	231	0.8719	10	0.89
11	nC_8	258	0.7068	5	0.98
12[C]	*p*-Xylene	281	0.8657	12	0.90
13[C]	*n*-Propylbenzene	319	0.8666	4	0.94
14	nC_{10}	345	0.7341	3	0.99
15[C]	*n*-Butylbenzene	362	0.8646	3	0.93
16[C]	nC_{12}	421	0.7526	3	1.00
17[C]	nC_{13}	456	0.7601	2	1.02
18	nC_{14}	486	0.7667	2	1.04
19	nC_{15}	519	0.7721	2	1.05

[A] "Selected Values of Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Project 44, Table 23-2, April 1956.

[B] Necessary if sample contains isopentane and lighter compounds.

[C] Necessary for system evaluation.

[D] Replace 2,4DMC_5 with benzene if sample contains more than 5 % benzene.

TABLE 3 Report Format

Percent Off	°F	Percent Off	°F
0.5 (IBP)		51	
1		52	
2		53	
3		54	
4		55	
5		56	
6		57	
7		58	
8		59	
9		60	
10		61	
11		62	
12		63	
13		64	
14		65	
15		66	
16		67	
17		68	
18		69	
19		70	
20		71	
21		72	
22		73	
23		74	
24		75	
25		76	
26		77	
27		78	
28		79	
29		80	
30		81	
31		82	
32		83	
33		84	
34		85	
35		86	
36		87	
37		88	
38		89	
39		90	
40		91	
41		92	
42		93	
43		94	
44		95	
45		96	
46		97	
47		98	
48		99	
49		99.5 (FBP)	
50			

Component	Volume Percent
n-C_3	
iso-C_4	
n-C_4	
iso-C_5	

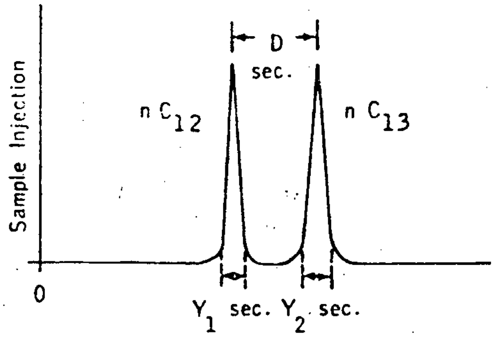


FIG. 1 Column Resolution.

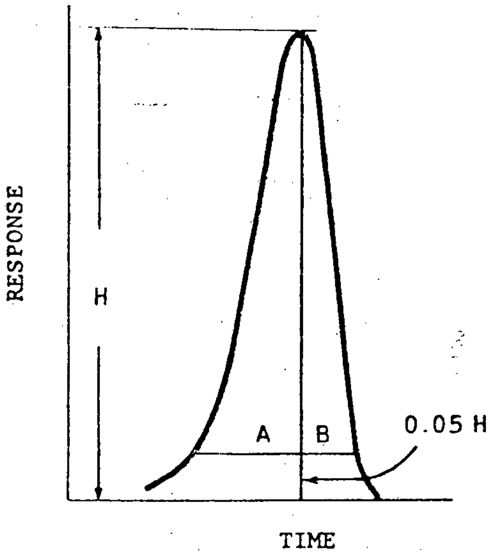


FIG. 2 Peak Skewness.

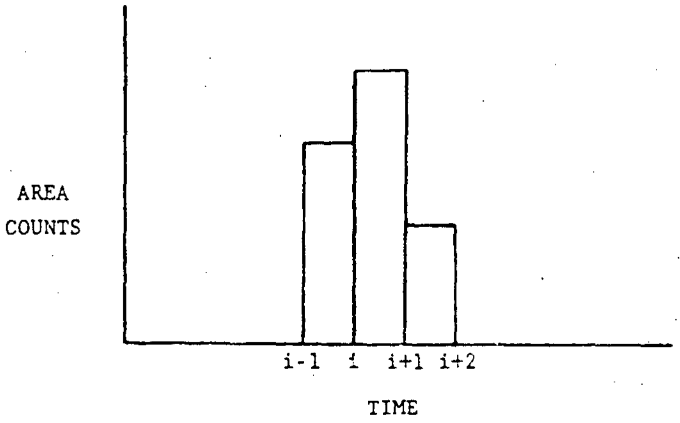


FIG. 3 Determination of Time to Peak Maxima.

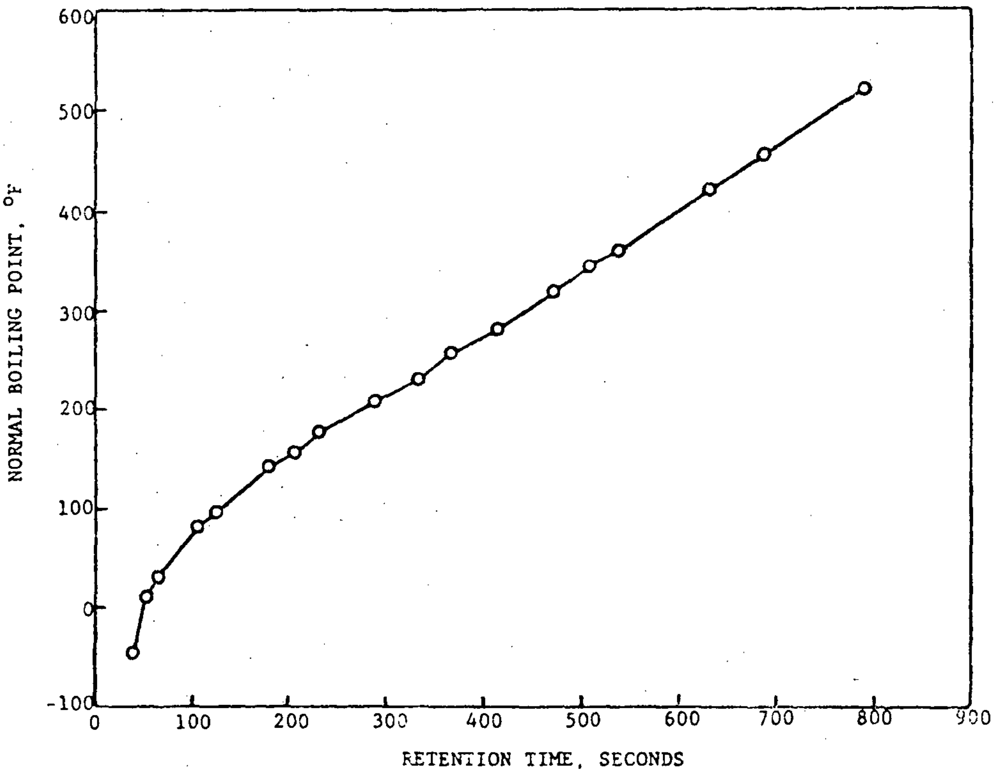


FIG. 4 Calibration Curve.

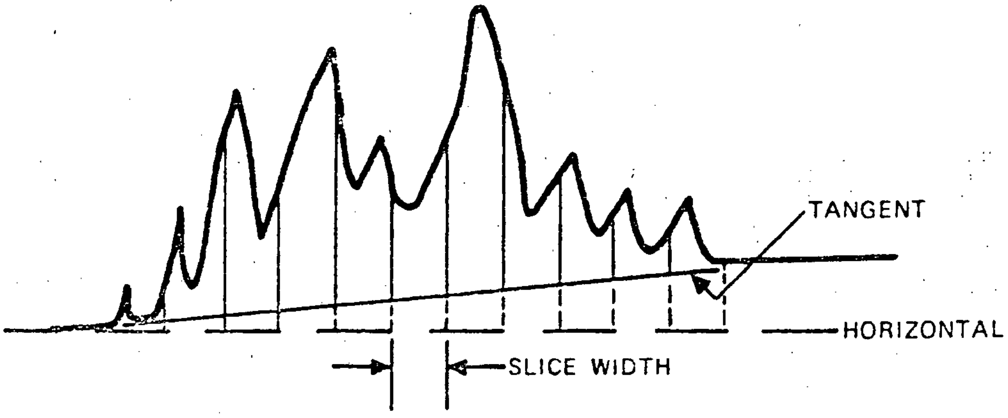


FIG. 5 GCD Drift Correction.

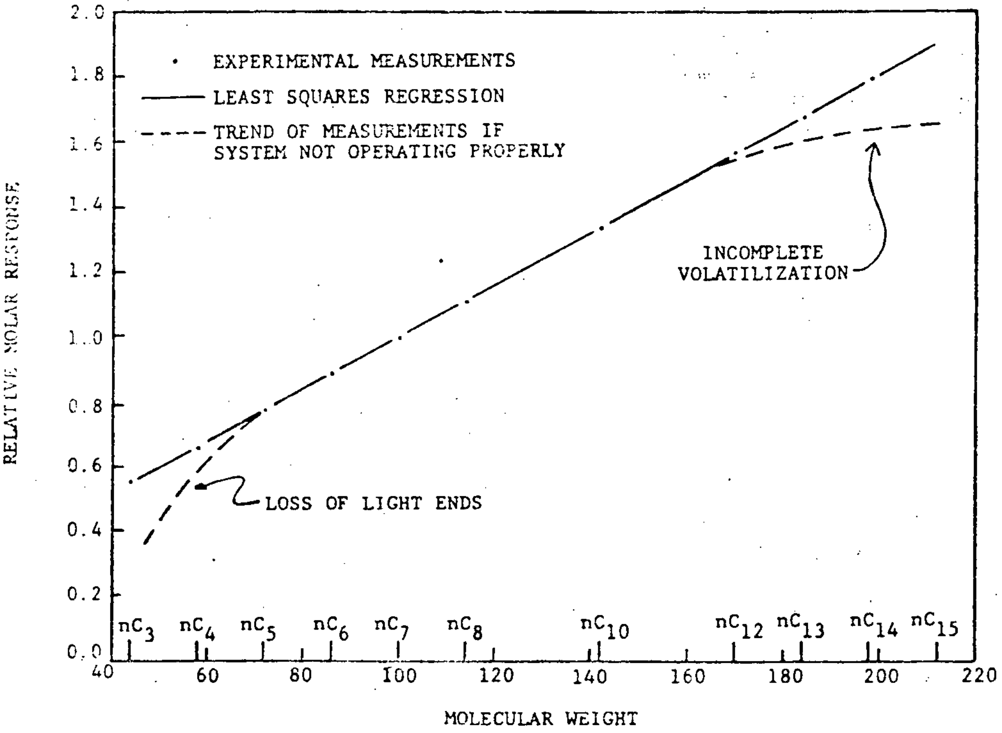


FIG. 6 Relative Molar Response versus Molecular Weight for *n*-Paraffins.

APPENDIX

X1. CALCULATION AND PREDICTION

X1.1 Results obtained by this method may be used to calculate the vapor pressure of the gasoline sample, including its Reid vapor pressure (RVP) and to predict the Method D 86 distillation curve.

X1.2 Calculate Reid vapor pressure by the following general equation:

$$\text{RVP} = \sum a V_i e^{-bt_i}$$

where:

V_i = volume fraction eluted in cut i,
t_i = boiling point of cut i, as determined from the calibration curve, and
a,b = empirically determined constants

X1.3 Predict Method D 86 distillation curve from the GCD boiling range distribution curve by an empirical correlation of the general form:

$$\text{Percent off, D } 86_i = \sum_i A_{ij} \times V_j$$

where:

A_{ij} = empirically determined constants and
V_j = percent off by GCD at cutpoint j.

```
SINGLE CHANNEL METHOD: CALIB.RT-1          9:44  20 MAR 84

SECTION 1: BASIC
PAGE 1
  ANALYSIS PARAMETERS
  CHANNEL: 1
  CALCULATION: A%
  AREA/HT: A
  STOP TIME:  23.33
  NUMB EXPECTED PKS:  200
  EQUILIBRATION TIME:  0
  UNRETAINED PK TIME:   0.00
  UNIDENT PK FACTOR: 1.000000
  SLICE WIDTH:   1

PAGE 2
  SAMPLE PARAMETERS
  RUN TYPE: L
  SAMPLE ID: STD. RT
  DIVISOR: 1.000000
  AMT STD: 7.500000
  MLTPLR: 1.000000

PAGE 3
  REPORT INSTRUCTIONS
  WHERE TO REPORT: L
  COPIES: 1
  TITLE: TEMPS DE RETENTION
  FORMAT: E
  DECIMAL PLACE: 4
  RESULT UNITS:
  REPORT UNIDENT PKS: Y
  REPORT INSTRUMENT CONDITIONS: N

PAGE 4
  PLOT INSTRUCTIONS
  PLOT: Y
  ZERO OFFSET:  5
  ANNOTATION
    RETENTION TIME: Y
    PLOT CONTROL: Y
    TIME TICKS: Y
    TIME EVENTS: Y
    PK START/END: N

PAGE 5
  CHART SPEED
    PAGES OR CM/MIN: C
    INIT VALUE:  1.0

PAGE 6
  PLOT ATTEN
    INIT PLOT ATTEN: 16


SECTION 2: TIME EVENTS
PAGE 1
   LINE#  TIME  EVENT   VALUE
   1       0.00  PR        100
   2       0.00  SN          2
   3       0.00  T%        5.0
   4       0.00  WI          4
   5       0.00  SB          5
```

```
SECTION 3: PEAK TABLE
PAGE 1
  STD PK#:   9
  RELATIVE RETEN PK#:   0
  RESOLUTION PK#:   0
  RESOLUTION MINIMUM:    0.0
  FACT%:   5.0
  IDENTIFICATION TIME WINDOWS +/-
  REF
    %: 10
    MIN:    0.00
  NON REF
    %:  5
    MIN:    0.00

PAGE 2


SECTION 4: GC INSTRUMENT CONTROL
PAGE 1
  COL TEMP
    ISO/INIT COL TEMP: -20
    INIT HOLD TIME:    0.00
   STEP#   FINAL TEMP   RATE   HOLD TIME
   1          190        9.0       0.00

PAGE 2
  DETECTORS
  DET A TYPE: TCD
  DET B TYPE:
   LN#  TIME SIDE ATTN RANGE ZERO
   1     0.00  A   64    .5    Y
   2     0.00  B               Y

PAGE 3
  TEMP/FLOW
  INJ A TEMP: 220
  INJ B TEMP: 220
  ION TEMP:    0
  TCD TEMP: 270
  TCD FIL TEMP: 290
  AUX TEMP:    0
  COL A FLOW: 60
  COL B FLOW: 60

PAGE 4


SECTION 7: POST RUN
PAGE 1
  FILE NAME: RT/
  SAVE INSTRUCTIONS
    TYPE: RAW
    WHERE TO SAVE: U
  TRANSMIT/REPLOT INSTRUCTIONS
    TRANSMIT RAW DATA: N
    REPLOT WITH BASELINES: N
    RAW DATA LOCATION: U
    TRANSMIT REPORT: Y

PAGE 2
  METHOD LINKING INSTRUCTIONS
    METHOD:
    LINK CALC RESULTS: N
  PROGRAM EXECUTION
    PROGRAM:
    PARAMETERS:
    RESERVE PRINTER: Y
```

```
SECTION 10: NOTE PAD
PAGE 1
   LINE#        VALUE
    1        COLONNE:SE-30 5% G.AIW DMCS (MESH:60/80)
    2        DIMENSIONS:5'X125"(O.D.)
    3        *VOLUME D'INJECTION: 1 MICROLITRE
    4        *GAZ PORTEUR: HELIUM

SECTION 11: BASELINE TIME/AMPLITUDE
PAGE 1
   LINE#  TIME   AMPLITUDE
    1        0.0          -2
    2        0.2          -4
    3        0.4          -7
    4        0.6          -7
```

```
SINGLE CHANNEL METHOD: CALIB.RT-2          9:47  20 MAR 84

SECTION 1: BASIC
PAGE 1
  ANALYSIS PARAMETERS
  CHANNEL: 1
  CALCULATION: A%
  AREA/HT: A
  STOP TIME:  23.33
  NUMB EXPECTED PKS:  200
  EQUILIBRATION TIME:  0
  UNRETAINED PK TIME:   0.00
  UNIDENT PK FACTOR: 1.000000
  SLICE WIDTH:   1

PAGE 2
  SAMPLE PARAMETERS
  RUN TYPE: L
  SAMPLE ID: STD. RT
  DIVISOR: 1.000000
  AMT STD: 7.500000
  MLTPLR: 1.000000

PAGE 3
  REPORT INSTRUCTIONS
  WHERE TO REPORT: L
  COPIES: 1
  TITLE: TEMPS DE RETENTION
  FORMAT: E
  DECIMAL PLACE: 4
  RESULT UNITS:
  REPORT UNIDENT PKS: Y
  REPORT INSTRUMENT CONDITIONS: N

PAGE 4
  PLOT INSTRUCTIONS
  PLOT: Y
  ZERO OFFSET:  5
  ANNOTATION
    RETENTION TIME: Y
    PLOT CONTROL: Y
    TIME TICKS: Y
    TIME EVENTS: Y
    PK START/END: N

PAGE 5
  CHART SPEED
    PAGES OR CM/MIN: C
    INIT VALUE:  1.0

PAGE 6
  PLOT ATTEN
    INIT PLOT ATTEN: 16

SECTION 2: TIME EVENTS
PAGE 1
   LINE#  TIME  EVENT   VALUE
   1       0.00  PR       1200
   2       0.00  SN          2
   3       0.00  T%        5.0
   4       0.00  WI          2
   5       0.00  SB          5
   6       1.45  WI          4
   7       3.00  PR       8000
   8       8.04  WI          8
```

```
SECTION 3: PEAK TABLE
PAGE 1
   STD PK#:   9
   RELATIVE RETEN PK#:   0
   RESOLUTION PK#:   0
   RESOLUTION MINIMUM:    0.0
   FACT%:    5.0
   IDENTIFICATION TIME WINDOWS +/-
   REF
     %: 10
     MIN:    0.00
   NON REF
     %:  5
     MIN:    0.00

PAGE 2
    PK# TIME   NAME              FACTOR    AMOUNT REF GR# MUST LO    MUST HI
     1    0.39                 0.000000 1.000000         0.000000 0.000000
     2    0.64                 0.000000 1.000000         0.000000 0.000000
     3    0.89                 0.000000 1.000000         0.000000 0.000000
     4    1.78                 0.000000 1.000000         0.000000 0.000000
     5    2.23                 0.000000 1.000000         0.000000 0.000000
     6    3.59                 0.000000 1.000000         0.000000 0.000000
     7    4.27                 0.000000 1.000000         0.000000 0.000000
     8    4.94                 0.000000 1.000000         0.000000 0.000000
     9    6.53                 0.000000 1.000000         0.000000 0.000000
     10   7.60                 0.000000 1.000000         0.000000 0.000000
     11   8.64                 0.000000 1.000000         0.000000 0.000000
     12   9.78                 0.000000 1.000000         0.000000 0.000000
     13  11.30                 0.000000 1.000000         0.000000 0.000000
     14  12.43                 0.000000 1.000000         0.000000 0.000000
     15  13.12                 0.000000 1.000000         0.000000 0.000000
     16  15.74                 0.000000 1.000000         0.000000 0.000000
     17  17.21                 0.000000 1.000000         0.000000 0.000000
     18  18.62                 0.000000 1.000000         0.000000 0.000000
     19  19.96                 0.000000 1.000000         0.000000 0.000000
     20  21.23                 0.000000 1.000000         0.000000 0.000000
     21  22.45                 0.000000 1.000000         0.000000 0.000000

SECTION 4: GC INSTRUMENT CONTROL
PAGE 1
  COL TEMP
    ISO/INIT COL TEMP: -20
    INIT HOLD TIME:   0.00
   STEP#   FINAL TEMP   RATE   HOLD TIME
   1          190        9.0       0.00

PAGE 2
  DETECTORS
  DET A TYPE: TCD
  DET B TYPE:
   LN#  TIME SIDE ATTN RANGE ZERO
   1     0.00  A   64    .5    Y
   2     0.00  B               Y

PAGE 3
  TEMP/FLOW
  INJ A TEMP: 220
  INJ B TEMP: 220
  ION TEMP:   0
  TCD TEMP: 270
  TCD FIL TEMP: 290
  AUX TEMP:   0
  COL A FLOW: 60
  COL B FLOW: 60

PAGE 4
```

```
SECTION 7: POST RUN
PAGE 1
  FILE NAME: RT/
  SAVE INSTRUCTIONS
    TYPE: RAW
    WHERE TO SAVE: U
  TRANSMIT/REPLOT INSTRUCTIONS
    TRANSMIT RAW DATA: N
    REPLOT WITH BASELINES: N
    RAW DATA LOCATION: U
    TRANSMIT REPORT: Y

PAGE 2
  METHOD LINKING INSTRUCTIONS
    METHOD:
    LINK CALC RESULTS: N
  PROGRAM EXECUTION
    PROGRAM:
    PARAMETERS:
    RESERVE PRINTER: Y


SECTION 10: NOTE PAD
PAGE 1
   LINE#        VALUE
   1        COLONNE:SE-30 5% G.AIW DMCS (MESH:60/80)
   2        DIMENSIONS:5'X125"(O.D.)
   3        *VOLUME D'INJECTION: 1 MICROLITRE
   4        *GAZ PORTEUR: HELIUM
```

```
SINGLE CHANNEL METHOD: CALIB.RRF-1          9:49  20 MAR 84

SECTION 1: BASIC
PAGE 1
  ANALYSIS PARAMETERS
  CHANNEL: 1
  CALCULATION: N%
  AREA/HT: A
  STOP TIME:  23.33
  NUMB EXPECTED PKS:  200
  EQUILIBRATION TIME:  0
  UNRETAINED PK TIME:   0.00
  UNIDENT PK FACTOR: 1.000000
  SLICE WIDTH:   1

PAGE 2
  SAMPLE PARAMETERS
  RUN TYPE: C
  SAMPLE ID: STD. RRF
  DIVISOR: 1.000000
  AMT STD: 7.500000
  MLTPLR: 1.000000

PAGE 3
  REPORT INSTRUCTIONS
  WHERE TO REPORT: L
  COPIES: 1
  TITLE: FACTEURS DE REPONSE RELATIVE
  FORMAT: E
  DECIMAL PLACE: 4
  RESULT UNITS:
  REPORT UNIDENT PKS: Y
  REPORT INSTRUMENT CONDITIONS: N

PAGE 4
  PLOT INSTRUCTIONS
  PLOT: Y
  ZERO OFFSET:  5
  ANNOTATION
    RETENTION TIME: Y
    PLOT CONTROL: Y
    TIME TICKS: Y
    TIME EVENTS: Y
    PK START/END: N

PAGE 5
  CHART SPEED
    PAGES OR CM/MIN: C
    INIT VALUE:  1.0

PAGE 6
  PLOT ATTEN
    INIT PLOT ATTEN: 16


SECTION 2: TIME EVENTS
PAGE 1
   LINE#  TIME  EVENT   VALUE
   1       0.00  PR      1200
   2       0.00  SN         2
   3       0.00  T%       5.0
   4       0.00  WI         2
   5       0.00  SB         5
   6       1.45  WI         4
   7       3.00  PR      8000
   8       8.04  WI         8
```

```
SECTION 3: PEAK TABLE
PAGE 1
  STD PK#:  6
  RELATIVE RETEN PK#:  0
  RESOLUTION PK#:  0
  RESOLUTION MINIMUM:   0.0
  FACT%:   5.0
  IDENTIFICATION TIME WINDOWS +/-
  REF
    %: 10
    MIN:   0.00
  NON REF
    %:  5
    MIN:   0.00

PAGE 2
   PK# TIME   NAME         FACTOR   AMOUNT REF GR# MUST LO   MUST HI
   1     1.79 *I-C5       0.000000 8.900000       0.000000 0.000000
   2     2.23 *N-C5       0.000000 7.600000       0.000000 0.000000
   3     3.60 *2MC5       0.000000 5.300000       0.000000 0.000000
   4     4.28 *N-C6       0.000000 4.900000       0.000000 0.000000
   5     4.96 *24DMC5     0.000000 5.300000       0.000000 0.000000
   6     6.54 *N-C7       1.000000 7.500000 R     0.000000 0.000000
   7     7.60 *TOLUENE.A  0.000000 8.650000       0.000000 0.000000
   8     8.66 *N-C8       0.000000 5.000000       0.000000 0.000000
   9     9.78 *P-XYLEN.A  0.000000 9.800000       0.000000 0.000000
   10   11.31 *PR-BENZ.A  0.000000 4.400000       0.000000 0.000000
   11   12.45 *N-C10      0.000000 3.100000       0.000000 0.000000
   12   13.15 *BU-BENZ.A  0.000000 2.900000       0.000000 0.000000
   13   15.76 *N-C12      0.000000 3.100000       0.000000 0.000000
   14   17.24 *N-C13      0.000000 2.000000       0.000000 0.000000
   15   18.66 *N-C14      0.000000 1.900000       0.000000 0.000000
   16   20.00 *N-C15      0.000000 2.000000       0.000000 0.000000
   17   21.27 *N-C16      0.000000 2.100000       0.000000 0.000000
   18   22.47 *N-C17      0.000000 2.300000       0.000000 0.000000

SECTION 4: GC INSTRUMENT CONTROL
PAGE 1
  COL TEMP
    ISO/INIT COL TEMP: -20
    INIT HOLD TIME:   0.00
   STEP#   FINAL TEMP   RATE   HOLD TIME
   1          190        9.0      0.00

PAGE 2
  DETECTORS
  DET A TYPE: TCD
  DET B TYPE:
   LN#  TIME SIDE ATTN RANGE ZERO
   1     0.00  A   64    .5    Y
   2     0.00  B               Y

PAGE 3
  TEMP/FLOW
  INJ A TEMP: 220
  INJ B TEMP: 220
  ION TEMP:   0
  TCD TEMP: 270
  TCD FIL TEMP: 290
  AUX TEMP:   0
  COL A FLOW: 60
  COL B FLOW: 60

PAGE 4
```

```
SECTION 7: POST RUN
PAGE 1
  FILE NAME: RRF/
  SAVE INSTRUCTIONS
    TYPE: RAW
    WHERE TO SAVE: U
  TRANSMIT/REPLOT INSTRUCTIONS
    TRANSMIT RAW DATA: N
    REPLOT WITH BASELINES: N
    RAW DATA LOCATION: U
    TRANSMIT REPORT: Y

PAGE 2
  METHOD LINKING INSTRUCTIONS
    METHOD:
    LINK CALC RESULTS: N
  PROGRAM EXECUTION
    PROGRAM:
    PARAMETERS:
    RESERVE PRINTER: Y


SECTION 10: NOTE PAD
PAGE 1
   LINE#        VALUE
   1          COLONNE:SE-30 5% G.AIW DMCS (MESH:60/80)
   2          DIMENSIONS:5'X125"(O.D.)
   3          *VOLUME D'INJECTION: 1 MICROLITRE
   4          *GAZ PORTEUR: HELIUM
```

```
SINGLE CHANNEL METHOD: CALIB.RRF-2         9:51  20 MAR 84

SECTION 1: BASIC
PAGE 1
  ANALYSIS PARAMETERS
  CHANNEL: 1
  CALCULATION: N%
  AREA/HT: A
  STOP TIME:  23.33
  NUMB EXPECTED PKS:  200
  EQUILIBRATION TIME:  0
  UNRETAINED PK TIME:   0.00
  UNIDENT PK FACTOR: 1.000000
  SLICE WIDTH:   1

PAGE 2
  SAMPLE PARAMETERS
  RUN TYPE: C
  SAMPLE ID: STD. RRF
  DIVISOR: 1.000000
  AMT STD: 7.500000
  MLTPLR: 1.000000

PAGE 3
  REPORT INSTRUCTIONS
  WHERE TO REPORT: L
  COPIES: 1
  TITLE: FACTEURS DE REPONSE RELATIVE
  FORMAT: E
  DECIMAL PLACE: 4
  RESULT UNITS:
  REPORT UNIDENT PKS: Y
  REPORT INSTRUMENT CONDITIONS: N

PAGE 4
  PLOT INSTRUCTIONS
  PLOT: Y
  ZERO OFFSET:  5
  ANNOTATION
    RETENTION TIME: Y
    PLOT CONTROL: Y
    TIME TICKS: Y
    TIME EVENTS: Y
    PK START/END: N

PAGE 5
  CHART SPEED
    PAGES OR CM/MIN: C
    INIT VALUE:  1.0

PAGE 6
  PLOT ATTEN
    INIT PLOT ATTEN: 16


SECTION 2: TIME EVENTS
PAGE 1
   LINE#  TIME  EVENT   VALUE
   1      0.00  PR       1200
   2      0.00  SN          2
   3      0.00  T%        5.0
   4      0.00  WI          2
   5      0.00  SB          5
   6      1.45  WI          4
   7      3.00  PR       8000
   8      8.04  WI          8
```

```
SECTION 3: PEAK TABLE
PAGE 1
  STD PK#:  6
  RELATIVE RETEN PK#:  0
  RESOLUTION PK#:  0
  RESOLUTION MINIMUM:   0.0
  FACT%:   5.0
  IDENTIFICATION TIME WINDOWS +/-
  REF
    %: 10
    MIN:   0.00
  NON REF
    %:  5
    MIN:   0.00

PAGE 2
   PK# TIME  NAME         FACTOR   AMOUNT REF GR# MUST LO   MUST HI
   1    1.79 *I-C5        1.508770 8.900000       0.000000 0.000000
   2    2.23 *N-C5        1.215630 7.600000       0.000000 0.000000
   3    3.60 *2MC5        1.000470 5.300000       0.000000 0.000000
   4    4.28 *N-C6        0.990242 4.900000       0.000000 0.000000
   5    4.96 *24DMC5      0.998199 5.300000       0.000000 0.000000
   6    6.54 *N-C7        1.000000 7.500000 R     0.000000 0.000000
   7    7.60 *TOLUENE.A 1.162070 8.650000       0.000000 0.000000
   8    8.66 *N-C8        0.825919 5.000000       0.000000 0.000000
   9    9.78 *P-XYLEN.A 1.121360 9.800000       0.000000 0.000000
   10  11.31 *PR-BENZ.A 0.953399 4.400000       0.000000 0.000000
   11  12.45 *N-C10       0.763491 3.100000       0.000000 0.000000
   12  13.15 *BU-BENZ.A 0.764883 2.900000       0.000000 0.000000
   13  15.76 *N-C12       0.749444 3.100000       0.000000 0.000000
   14  17.24 *N-C13       0.652485 2.000000       0.000000 0.000000
   15  18.66 *N-C14       0.628721 1.900000       0.000000 0.000000
   16  20.00 *N-C15       0.594913 2.000000       0.000000 0.000000
   17  21.27 *N-C16       0.684486 2.100000       0.000000 0.000000
   18  22.47 *N-C17       0.779191 2.300000       0.000000 0.000000

SECTION 4: GC INSTRUMENT CONTROL
PAGE 1
  COL TEMP
    ISO/INIT COL TEMP: -20
    INIT HOLD TIME:   0.00
   STEP#   FINAL TEMP   RATE   HOLD TIME
   1         190         9.0      0.00

PAGE 2
  DETECTORS
  DET A TYPE: TCD
  DET B TYPE:
   LN#  TIME SIDE ATTN RANGE ZERO
   1     0.00  A   64    .5    Y
   2     0.00  B               Y

PAGE 3
  TEMP/FLOW
  INJ A TEMP: 220
  INJ B TEMP: 220
  ION TEMP:   0
  TCD TEMP: 270
  TCD FIL TEMP: 290
  AUX TEMP:   0
  COL A FLOW: 60
  COL B FLOW: 60

PAGE 4
```

```
SECTION 7: POST RUN
PAGE 1
  FILE NAME: RRF/
  SAVE INSTRUCTIONS
    TYPE: RAW
    WHERE TO SAVE: U
  TRANSMIT/REPLOT INSTRUCTIONS
    TRANSMIT RAW DATA: N
    REPLOT WITH BASELINES: N
    RAW DATA LOCATION: U
    TRANSMIT REPORT: Y

PAGE 2
  METHOD LINKING INSTRUCTIONS
    METHOD:
    LINK CALC RESULTS: N
  PROGRAM EXECUTION
    PROGRAM:
    PARAMETERS:
    RESERVE PRINTER: Y

SECTION 10: NOTE PAD
PAGE 1
   LINE#       VALUE
    1       COLONNE:SE-30 5% G.AIW DMCS (MESH:60/80)
    2       DIMENSIONS:5'X125"(O.D.)
    3       *VOLUME D'INJECTION: 1 MICROLITRE
    4       *GAZ PORTEUR: HELIUM
```

```
SINGLE CHANNEL METHOD: ANALYSE           9:53  20 MAR 84

SECTION 1: BASIC
PAGE 1
  ANALYSIS PARAMETERS
  CHANNEL: 1
  CALCULATION: SL
  AREA/HT: A
  STOP TIME:  23.33
  NUMB EXPECTED PKS:  200
  EQUILIBRATION TIME:  0
  UNRETAINED PK TIME:   0.00
  UNIDENT PK FACTOR: 1.000000
  SLICE WIDTH:   1

PAGE 2
  SAMPLE PARAMETERS
  RUN TYPE: A
  SAMPLE ID: ECH.#??
  DIVISOR: 1.000000
  AMT STD: 7.500000
  MLTPLR: 1.000000

PAGE 3
  REPORT INSTRUCTIONS
  WHERE TO REPORT: L
  COPIES: 1
  TITLE: DIST.SIMULEE D-3710
  FORMAT: E
  DECIMAL PLACE: 4
  RESULT UNITS:
  REPORT UNIDENT PKS: Y
  REPORT INSTRUMENT CONDITIONS: N

PAGE 4
  PLOT INSTRUCTIONS
  PLOT: Y
  ZERO OFFSET:  5
  ANNOTATION
    RETENTION TIME: Y
    PLOT CONTROL: Y
    TIME TICKS: Y
    TIME EVENTS: Y
    PK START/END: N

PAGE 5
  CHART SPEED
    PAGES OR CM/MIN: C
    INIT VALUE:  1.0

PAGE 6
  PLOT ATTEN
    INIT PLOT ATTEN: 16


SECTION 2: TIME EVENTS
PAGE 1
   LINE#  TIME  EVENT   VALUE
   1      0.00  PR       1200
   2      0.00  SN          2
   3      0.00  T%        5.0
   4      0.00  WI          2
   5      0.00  SB          5
   6      1.45  WI          4
   7      3.00  PR       8000
   8      8.04  WI          8
```

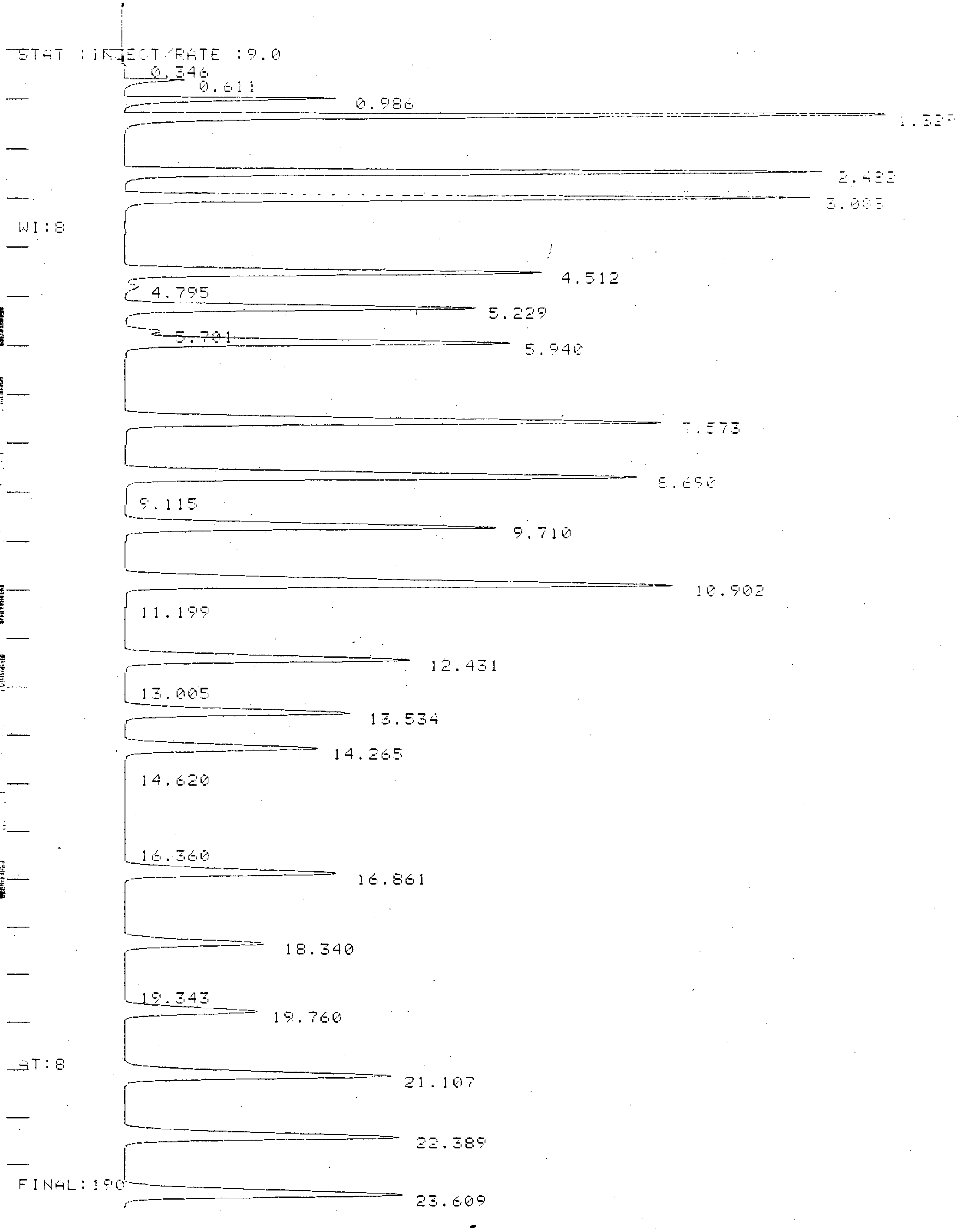
```
SECTION 3: PEAK TABLE
PAGE 1
  STD PK#:  6
  RELATIVE RETEN PK#:  0
  RESOLUTION PK#:  0
  RESOLUTION MINIMUM:   0.0
  FACT%:   5.0
  IDENTIFICATION TIME WINDOWS +/-
  REF
    %: 10
    MIN:   0.00
  NON REF
    %:  5
    MIN:   0.00

PAGE 2
   PK# TIME  NAME         FACTOR   AMOUNT REF GR# MUST LO   MUST HI
   1    1.79 *I-C5       1.508770 8.900000        0.000000 0.000000
   2    2.23 *N-C5       1.215630 7.600000        0.000000 0.000000
   3    3.60 *2MC5       1.000470 5.300000        0.000000 0.000000
   4    4.28 *N-C6       0.990242 4.900000        0.000000 0.000000
   5    4.96 *24DMC5     0.998199 5.300000        0.000000 0.000000
   6    6.54 *N-C7       1.000000 7.500000 R      0.000000 0.000000
   7    7.60 *TOLUENE.A  1.162070 8.650000        0.000000 0.000000
   8    8.66 *N-C8       0.825919 5.000000        0.000000 0.000000
   9    9.78 *P-XYLEN.A  1.121360 9.800000        0.000000 0.000000
   10  11.31 *PR-BENZ.A  0.953399 4.400000        0.000000 0.000000
   11  12.45 *N-C10      0.763491 3.100000        0.000000 0.000000
   12  13.15 *BU-BENZ.A  0.764883 2.900000        0.000000 0.000000
   13  15.76 *N-C12      0.749444 3.100000        0.000000 0.000000
   14  17.24 *N-C13      0.652485 2.000000        0.000000 0.000000
   15  18.66 *N-C14      0.628721 1.900000        0.000000 0.000000
   16  20.00 *N-C15      0.594913 2.000000        0.000000 0.000000
   17  21.27 *N-C16      0.684486 2.100000        0.000000 0.000000
   18  22.47 *N-C17      0.779191 2.300000        0.000000 0.000000

SECTION 4: GC INSTRUMENT CONTROL
PAGE 1
  COL TEMP
    ISO/INIT COL TEMP: -20
    INIT HOLD TIME:   0.00
   STEP#   FINAL TEMP   RATE   HOLD TIME
   1          190        9.0      0.00

PAGE 2
  DETECTORS
  DET A TYPE: TCD
  DET B TYPE:
   LN#  TIME SIDE ATTN RANGE ZERO
   1     0.00  A   64    .5     Y
   2     0.00  B                Y

PAGE 3
  TEMP/FLOW
  INJ A TEMP: 220
  INJ B TEMP: 220
  ION TEMP:   0
  TCD TEMP: 270
  TCD FIL TEMP: 290
  AUX TEMP:   0
  COL A FLOW: 60
  COL B FLOW: 60

PAGE 4
```

```
SECTION 7: POST RUN
PAGE 1
  FILE NAME: ECH.#??
  SAVE INSTRUCTIONS
    TYPE: RAW
    WHERE TO SAVE: U
  TRANSMIT/REPLOT INSTRUCTIONS
    TRANSMIT RAW DATA: N
    REPLOT WITH BASELINES: N
    RAW DATA LOCATION: U
    TRANSMIT REPORT: Y

PAGE 2
  METHOD LINKING INSTRUCTIONS
    METHOD:
    LINK CALC RESULTS: N
  PROGRAM EXECUTION
    PROGRAM:
    PARAMETERS:
    RESERVE PRINTER: Y


SECTION 10: NOTE PAD
PAGE 1
   LINE#       VALUE
   1          COLONNE:SE-30 5% G.AIW DMCS (MESH:60/80)
   2          DIMENSIONS:5'X125"(O.D.)
   3          *VOLUME D'INJECTION: 1 MICROLITRE
   4          *GAZ PORTEUR: HELIUM
```

```
       VARIAN VISTA 401 - APPLE II
         SIMULATED DISTILLATION
---------------------------------------
METHOD: D3710/RT
ASTM METHOD TYPE: D3710


CALIBRATION
  OPERATOR   DENIS BOUDREAU
  TEMPERATURE UNIT    F
  CALIBRATION TYPE   1
  STANDARD PEAK #   9
  START PEAK #   4
  VOL% OR WT%   V

ANALYSIS
  OPERATOR   DENIS BOUDREAU
  PERCENT OFF  INTERVALS   5
  D-86  CORRELATIONS   Y
  REID VAPOR PRESSURE   Y

REPORT
 OUTPUT:
  CALIBRATION PLOT   Y
  ANALYSIS PLOT   Y
 INSTRUMENT CONDITIONS:
  COLUMN   5'X.125",SE-30(5%),60/80
  DETECTOR   TCD
  FLOW RATE   60 ML/MIN
  CARRIER GAS   HELIUM
  TEMP. PROGRAM   -20/9/190
  INJ. VOLUME   1 MICROLITERS




PEAK TABLE
PK# B.P.   PK.NAME   S.G.   VOL%  M.W.   R.T.   R.R.F.
--- ------ --------- ------ ----- ------ ------ ------
  1  -43.7 C3        0.5077 1.00   44.1     .39  1.000
  2   10.9 I-C4      0.5631 2.80   58.1     .64  1.000
  3   31.1 N-C4      0.5844 9.30   58.1     .89  1.000
  4   82.1 I-C5      0.6248 8.90   72.1    1.79  1.000
  5   96.9 N-C5      0.6312 7.60   72.1    2.23  1.000
  6  140.5 2-MEC5    0.6579 5.30   86.2    3.60  1.000
  7  155.7 N-C6      0.6640 4.90   86.2    4.28  1.000
  8  176.9 24-DMC5   0.6772 5.30  100.2    4.96  1.000
  9  209.2 N-C7      0.6882 7.50  100.2    6.54  1.000
 10  231.1 TOLUENE.A 0.8719 8.65   92.1    7.60  1.000
 11  258.2 N-C8      0.7068 5.00  114.2    8.66  1.000
 12  281.0 P-XYLEN.A 0.8657 9.80  106.2    9.78  1.000
 13  318.6 PR-BENZ.A 0.8666 4.40  120.2   11.31  1.000
 14  345.4 N-C10     0.7341 3.10  142.3   12.45  1.000
 15  361.9 BU-BENZ.A 0.8646 2.90  134.2   13.15  1.000
 16  421.3 N-C12     0.7526 3.10  170.3   15.76  1.000
 17  455.8 N-C13     0.7601 2.00  184.4   17.24  1.000
 18  488.4 N-C14     0.7667 1.90  198.4   18.66  1.000
 19  519.1 N-C15     0.7721 2.00  212.4   20.00  1.000
 20  548.6 N-C16     0.7765 2.10  226.4   21.27  1.000
 21  575.3 N-C17     0.7799 2.30  240.5   22.47  1.000
```

```
      VARIAN VISTA 401 - APPLE II
        SIMULATED DISTILLATION
----------------------------------------
METHOD: D3710/RRF/ANALYSE
ASTM METHOD TYPE: D3710


CALIBRATION
  OPERATOR   DENIS BOUDREAU
  TEMPERATURE UNIT     F
  CALIBRATION TYPE   2
  STANDARD PEAK #   9
  START PEAK #   4
  VOL% OR WT%   V

ANALYSIS
  OPERATOR   DENIS BOUDREAU
  PERCENT OFF  INTERVALS   5
  D-86  CORRELATIONS   Y
  REID VAPOR PRESSURE   Y

REPORT
 OUTPUT:
  CALIBRATION PLOT   Y
  ANALYSIS PLOT   Y
 INSTRUMENT CONDITIONS:
  COLUMN   5'X.125",SE-30(5%),60/80
  DETECTOR   TCD
  FLOW RATE   60 ML/MIN
  CARRIER GAS   HELIUM
  TEMP. PROGRAM   -20/9/190
  INJ. VOLUME   1 MICROLITERS



PEAK TABLE
PK# B.P.   PK.NAME   S.G.   VOL%  M.W.   R.T.   R.R.F.
--- ------ --------- ------ ----- ------ ------ ------
  1  -43.7 C3        0.5077  1.00   44.1    .39  1.064
  2   10.9 I-C4      0.5631  2.80   58.1    .64  1.057
  3   31.1 N-C4      0.5844  9.30   58.1    .89  1.019
  4   82.1 I-C5      0.6248  8.90   72.1   1.79  1.509
  5   96.9 N-C5      0.6312  7.60   72.1   2.23  1.216
  6  140.5 2-MEC5    0.6579  5.30   86.2   3.60  1.001
  7  155.7 N-C6      0.6640  4.90   86.2   4.28   .990
  8  176.9 24-DMC5   0.6772  5.30  100.2   4.96   .998
  9  209.2 N-C7      0.6882  7.50  100.2   6.54  1.000
 10  231.1 TOLUENE.A 0.8719  8.65   92.1   7.60  1.162
 11  258.2 N-C8      0.7068  5.00  114.2   8.66   .826
 12  281.0 P-XYLEN.A 0.8657  9.80  106.2   9.78  1.121
 13  318.6 PR-BENZ.A 0.8666  4.40  120.2  11.31   .953
 14  345.4 N-C10     0.7341  3.10  142.3  12.45   .764
 15  361.9 BU-BENZ.A 0.8646  2.90  134.2  13.15   .765
 16  421.3 N-C12     0.7526  3.10  170.3  15.76   .749
 17  455.8 N-C13     0.7601  2.00  184.4  17.24   .653
 18  488.4 N-C14     0.7667  1.90  198.4  18.66   .629
 19  519.1 N-C15     0.7721  2.00  212.4  20.00   .595
 20  548.6 N-C16     0.7765  2.10  226.4  21.27   .685
 21  575.3 N-C17     0.7799  2.30  240.5  22.47   .779
```

CHART SPEED 1.0 CM/MIN
ATTEN: [illegible] ZERO: 5% 1 MIN/TICK



```
TITLE: TEMPS DE RETENTION                          10:09    15 MAR 84

CHANNEL NO: 1      SAMPLE: STD.RT            METHOD: CALIB.RT-1

PEAK  PEAK            RESULT     TIME        TIME         AREA    SEP      W1/2
 NO   NAME                      (MIN)        OFFSET       COUNTS  CODE     (SEC)
   1                  0.0292     0.346                       350   BV        3.25
   2                  0.4521     0.611                      5415   VV        3.50
   3                  1.7743     0.986                     21251   VV        4.30
   4                  7.7394     1.629                     92694   VB        4.75
   5                  7.7140     2.482                     92390   BV        6.20
   6                  7.6606     3.008                     91751   VB      ? 6.30
   7                  5.4298     4.512                     65033   BV        7.25
   8                  0.1329     4.795                      1592   T         7.30
   9                  4.5670     5.229                     54699   VV        7.25
  10                  0.4155     5.701                      4976   VV        7.10
  11                  5.3851     5.940                     64497   VB        7.75
  12                  8.3647     7.573                    100183   BB        8.85
  13                  8.3397     8.690                     99884   BV        9.30
  14                  0.0091     9.115                       109   T        10.35
  15                  5.6587     9.710                     67774   VB        8.60
  16                  9.9627    10.902                    119323   BV       10.40
  17                  4.5188    12.431                     54121   BV        8.95
  18                  3.5327    13.534                     42311   VV        8.75
  19                  3.0167    14.265                     36131   VV        8.65
  20                  0.0134    16.360                       160   BV        9.20
  21                  3.4839    16.861                     41726   VB        9.20
  22                  2.2773    18.340                     27275   BB        9.10
  23                  2.2259    19.760                     26659   VB        9.30
  24                  2.3645    21.107                     28320   BB        9.70
  25                  2.3802    22.389                     28507   BB        9.70
  26                  2.5519    23.609                     30564   BB       10.30

TOTALS:            100.0000                              1197700

DETECTED PKS:     30      REJECTED PKS:      4

MULTIPLIER: 1.00000

NOISE:     1.2   OFFSET:      -2

NOTES:
   COLONNE:SE-30 5% G.AIW DMCS (MESH:60/80)
   DIMENSIONS:5'X125"(O.D.)
   *VOLUME D'INJECTION: 1 MICROLITRE
   *GAZ PORTEUR: HELIUM
```

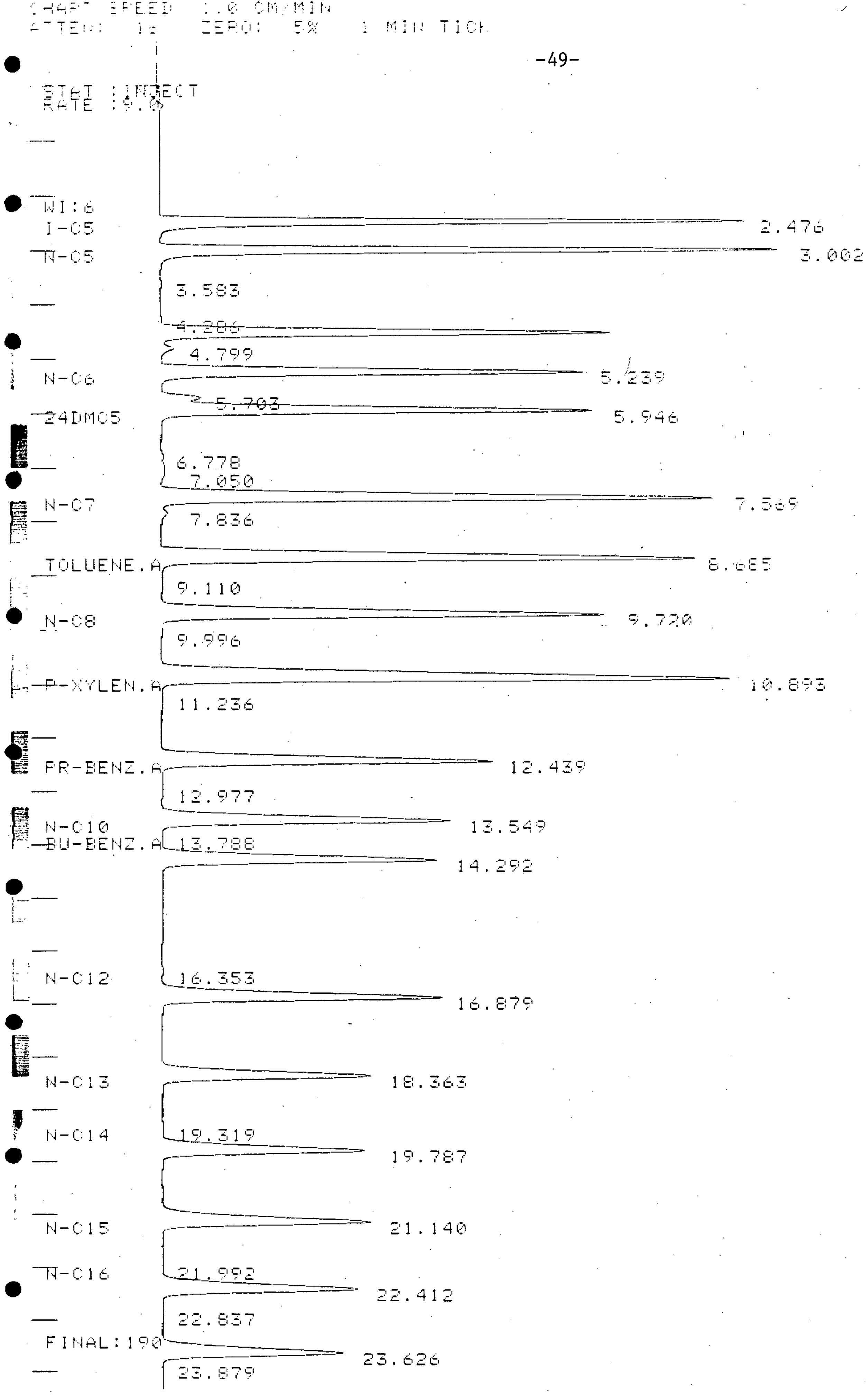
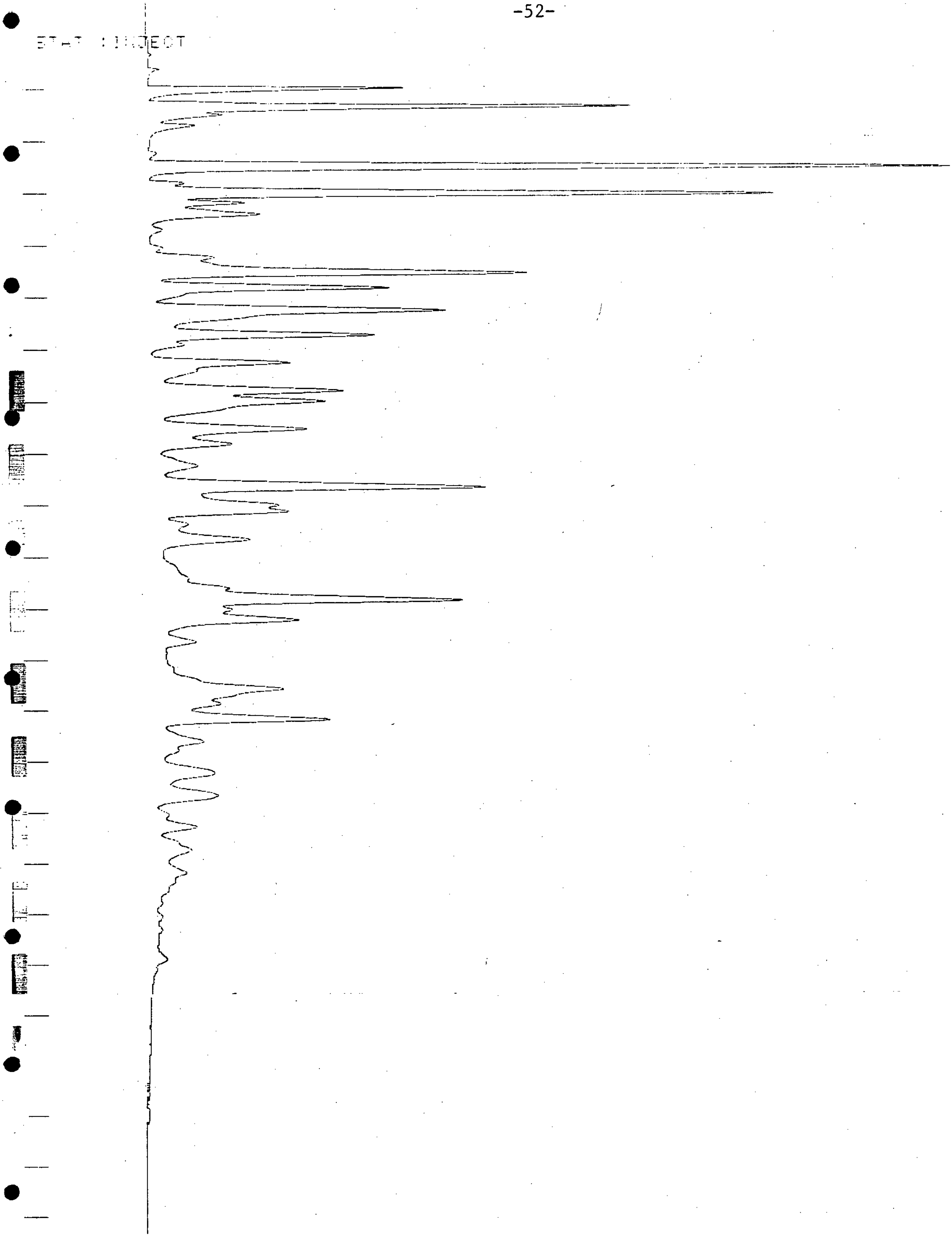


CHART SPEED 1.0 CM/MIN
ATTEN: 16 ZERO: 5% 1 MIN TICK
STAT :INJECT
RATE :9.0
WI:6
I-C5
2.476
N-C5
3.002
3.583
~~4.206~~
4.799
N-C6
5.239
~~5.703~~
24DMC5
5.946
6.778
7.050
N-C7
7.569
7.836
TOLUENE.A
8.685
9.110
N-C8
9.720
9.996
P-XYLEN.A
10.893
11.236
PR-BENZ.A
12.439
12.977
N-C10
13.549
BU-BENZ.A
13.788
14.292
N-C12
16.353
16.879
N-C13
18.363
N-C14
19.319
19.787
N-C15
21.140
N-C16
21.992
22.412
22.837
FINAL:190
23.626
23.879

```
TITLE:  FACTEURS DE  REPONSE RELATIVE                    11:16    15 MAR 84

CHANNEL NO: 1       SAMPLE: STD.RRF           METHOD: CALIB.RT-1

PEAK  PEAK          RESULT      TIME        TIME         AREA    SEP       W1/2
 NO   NAME          FACTOR      (MIN)       OFFSET/      COUNTS  CODE      (SEC)
   1  I-C5         1.532510U    2.476      -0.004        71146   BV         6.20
   2  N-C5         1.227940U    3.002      -0.008        75823   VV         6.30
   3  2MC5         1.007580U    4.516       0.006        64441   VV     ?   6.55
   4  N-C6         0.989270U    5.239       0.009        60680   VV     ?   7.25
   5  24DMC5       0.996061U    5.946       0.006        65186   VB     ?   7.50
   6  N-C7         1.000000U    7.569R     -0.001        91881   VV     ?   8.00
   7  TOLUENE.A    1.139550U    8.685      -0.005        92992   BV     ?   8.10
   8  N-C8         0.817701U    9.720       0.010        74510   VV     ?   8.05
   9  P-XYLEN.A    1.099170U   10.893      -0.007       109226   BV     ?   8.25
  10  PR-BENZ.A    0.929419U   12.439       0.009        57997   BV     ?   8.35
  11  N-C10        0.752655U   13.549       0.019        50458   VV     ?   8.40
  12  BU-BENZ.A    0.741667U   14.292       0.022        47502   VB     ?   8.35
  13  N-C12        0.739754U   16.879       0.019        51338   VB     ?   8.10
  14  N-C13        0.647625U   18.363       0.023        37833   BB     ?   8.70
  15  N-C14        0.619336U   19.787       0.027        37583   VB     ?   8.85
  16  N-C15        0.596364U   21.140       0.030        41085   BB     ?   9.20
  17  N-C16        0.678393U   22.412       0.022        37923   VV     ?   9.15
  18  N-C17        0.763145U   23.626       0.016        36922   BV     ?   9.60

TOTALS:                                     0.193     1105330

DETECTED PKS:     39       REJECTED PKS:      21

AMT STD: 7.50000      MULTIPLIER: 1.00000

NOISE:     2.4    OFFSET:      -2

SAVED FILE: CALIB.RRF000

NOTES:
   COLONNE:SE-30 5% G.AIW DMCS (MESH:60/80)
   DIMENSIONS:5'X125"(O.D.)
   *VOLUME D'INJECTION: 1 MICROLITRE
   *GAZ PORTEUR: HELIUM
```

```
       VARIAN VISTA 401 - APPLE II

          SIMULATED DISTILLATION
  ------------------------------------
  METHOD READY:


   METHOD: D3710

   MODE: CALIBRATION



                        SIMDIS CALIBRATION REPORT
                        -------------------------

 TITLE: FACTEURS DE REPONSE RELATIVE

 VISTA 401 METHOD: CALIB.RT-1          SIMDIS METHOD: D3710

 STANDARD ID: STD.RRF                  COLUMN: 5'X.125",SE-30(5%),60/80

 DATE: 11:16   MAR 16  '84             DETECTOR: TCD

 OPERATOR: DENIS BOUDREAU              TEMP PROGRAM: -20/9/190

 FLOW RATE: 30 ML / MIN                INJ. VOLUME: 1 MICROLITERS

 ASTM METHOD: D-3710                   CALIBRATION TYPE: R.R.F.

 PEAKS IN TABLE: 21                    INDENTIFIED PEAKS RECEIVED: 18



     PK#      PEAK ID.        B.P.         R.T.         R.R.F.
     ---     ----------    ----------   ----------   ----------

       1          C3          -43.7          .61        1.064
       2        I-C4           10.9          .99        1.057
       3        N-C4           31.1         1.33        1.019
   *   4        I-C5           82.1         2.48        1.533
       5        N-C5           96.9         3.01        1.228
       6      2-MEC5          140.5         4.51        1.008
       7        N-C6          155.7         5.23         .989
       8     24-DMC5          176.9         5.94         .996
  **   9        N-C7          209.2         7.57            1
      10   TOLUENE.A          231.1         8.69         1.14
      11        N-C8          258.2         9.71         .818
      12   P-XYLEN.A            281         10.9        1.099
      13   PR-BENZ.A          318.6        12.43         .929
      14       N-C10          345.4        13.53         .753
      15   BU-BENZ.A          361.9        14.27         .742
      16       N-C12          421.3        16.86          .74
      17       N-C13          455.8        18.34         .648
      18       N-C14          488.4        19.76         .619
      19       N-C15          519.1        21.11         .596
      20       N-C16          548.6        22.39         .678
      21       N-C17          575.3        23.61         .763

   *  R.R.F. QUANTITATIVE START PEAK
  **  R.R.F. STANDARD PEAK
```

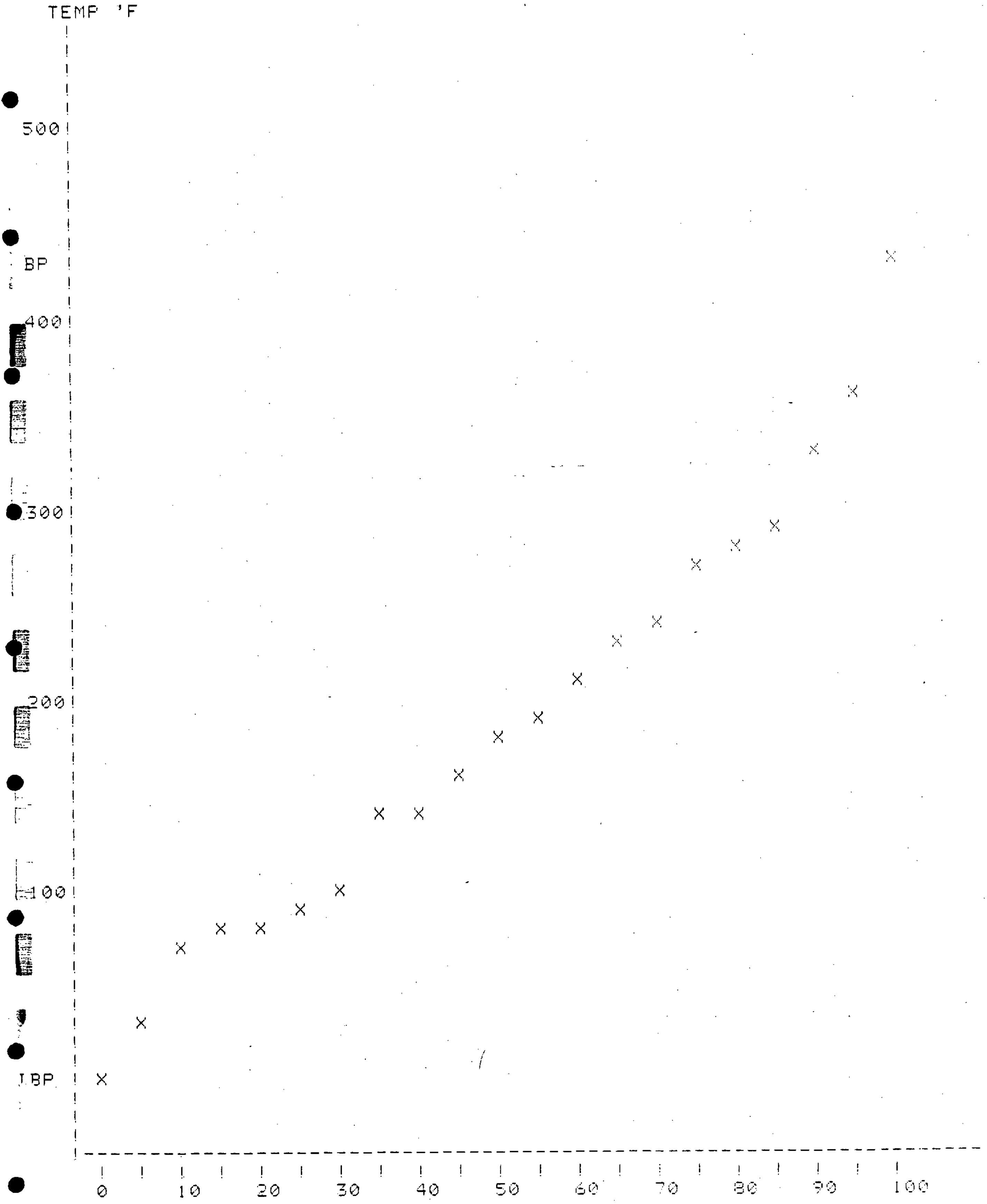
CHART SPEED 1.0 CM/MIN
ATTEN: 16 ZERO: 5% 1 MIN/TICK



```
       VARIAN VISTA 401 - APPLE II

          SIMULATED DISTILLATION
 ---------------------------------------
 METHOD READY:


  METHOD: D3710

  MODE: ANALYSIS




                              SIMDIS ANALYSIS REPORT
                              ---------------------

TITLE: ECH.#M-484

VISTA 401 METHOD: CALIB.RT-1          SIMDIS METHOD: D3710

SAMPLE ID: ECH.#M-484                 COLUMN: 5'X.125".SE-30(5%).60/80

DATE: 11:53   MAR 16  '84             DETECTOR: TCD

OPERATOR: DENIS BOUDREAU              TEMP PROGRAM: -20/9/190

FLOW RATE: 30 ML / MIN                INJ. VOLUME: 1 MICROLITERS

ASTM METHOD: D-3710                   CALIBRATION TYPE: R.T. & R.R.F.



                PERCENT OFF          B.P. (DEG. F)
                -----------          -------------

                    IBP                  5.1
                      5                 33.2
                     10                 79.2
                     15                 82
                     20                 87.5
                     25                 96.8
                     30                107.1
                     35                140.1
                     40                149.8
                     45                164.1
                     50                186.3
                     55                198.8
                     60                215.4
                     65                230.1
                     70                242
                     75                274.7
                     80                281.3
                     85                299.4
                     90                330.3
                     95                367.1
                    FBP                430.7

 -----------------------------------------------------------


                 COMPONENT          VOLUME PERCENT
                 ---------          --------------

                 C3                           1.16
                 I-C4                         3.14
                 N-C4                         3.65
```

```
---------------------------------------------------------------------


REID VAPOR PRESSURE:   18.61



                     D-86 CORRELATION
                     ----------------

            PERCENT OFF              B.P. (DEG./F)
            -----------              -------------

                IBP                    94.49
                 10                   112.78
                 20                   116.05
                 30                   132.06
                 50                   186.66
                 70                   238.48
                 80                   274.92
                 90                   318.18
                FBP                   395.94
```

ANALYSIS PLOT



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LAST SLICE AREA = -13
SUM OF AREA = 1331118
SLICE WIDTH = 10 SEC.
END POINT SL#= 1290
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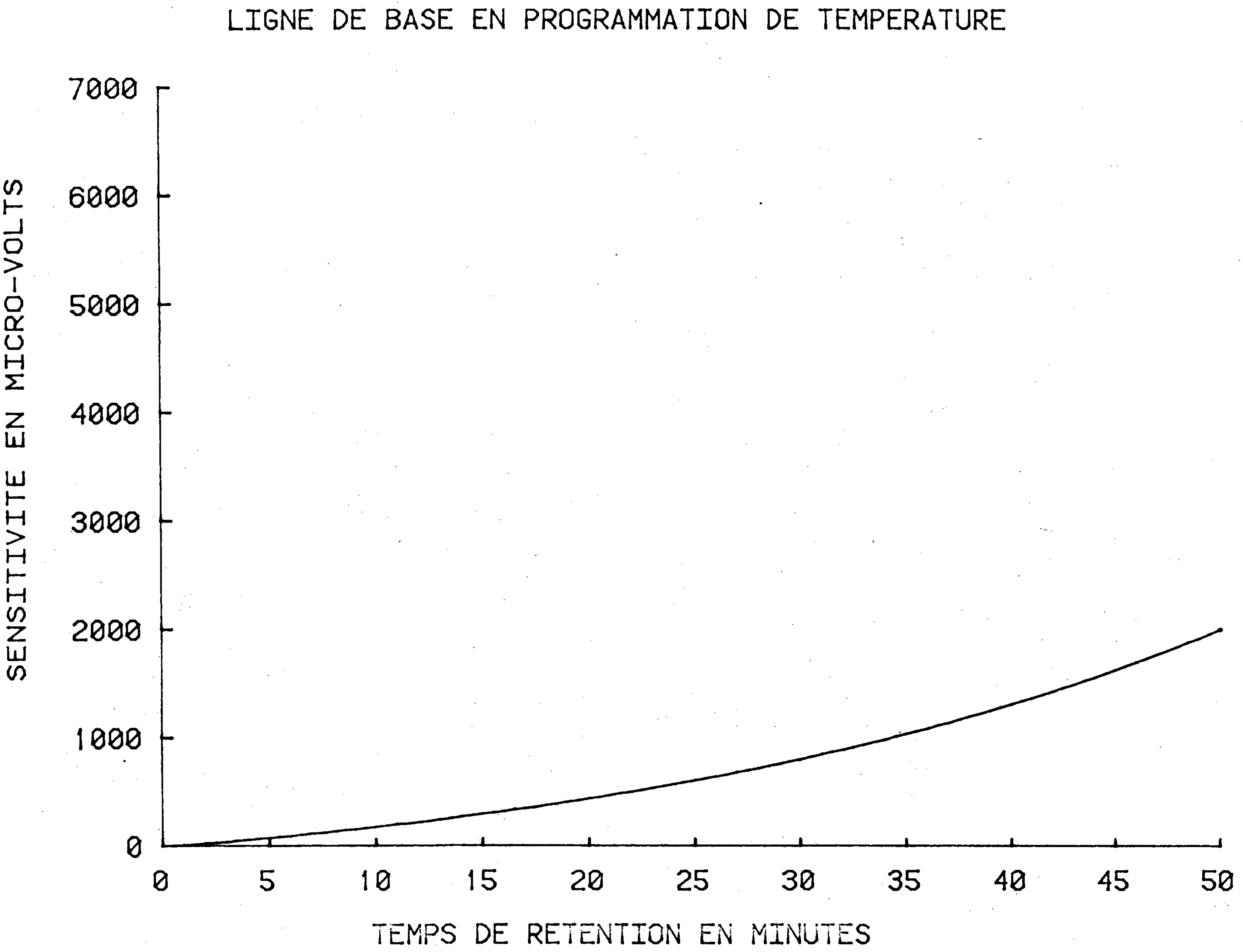
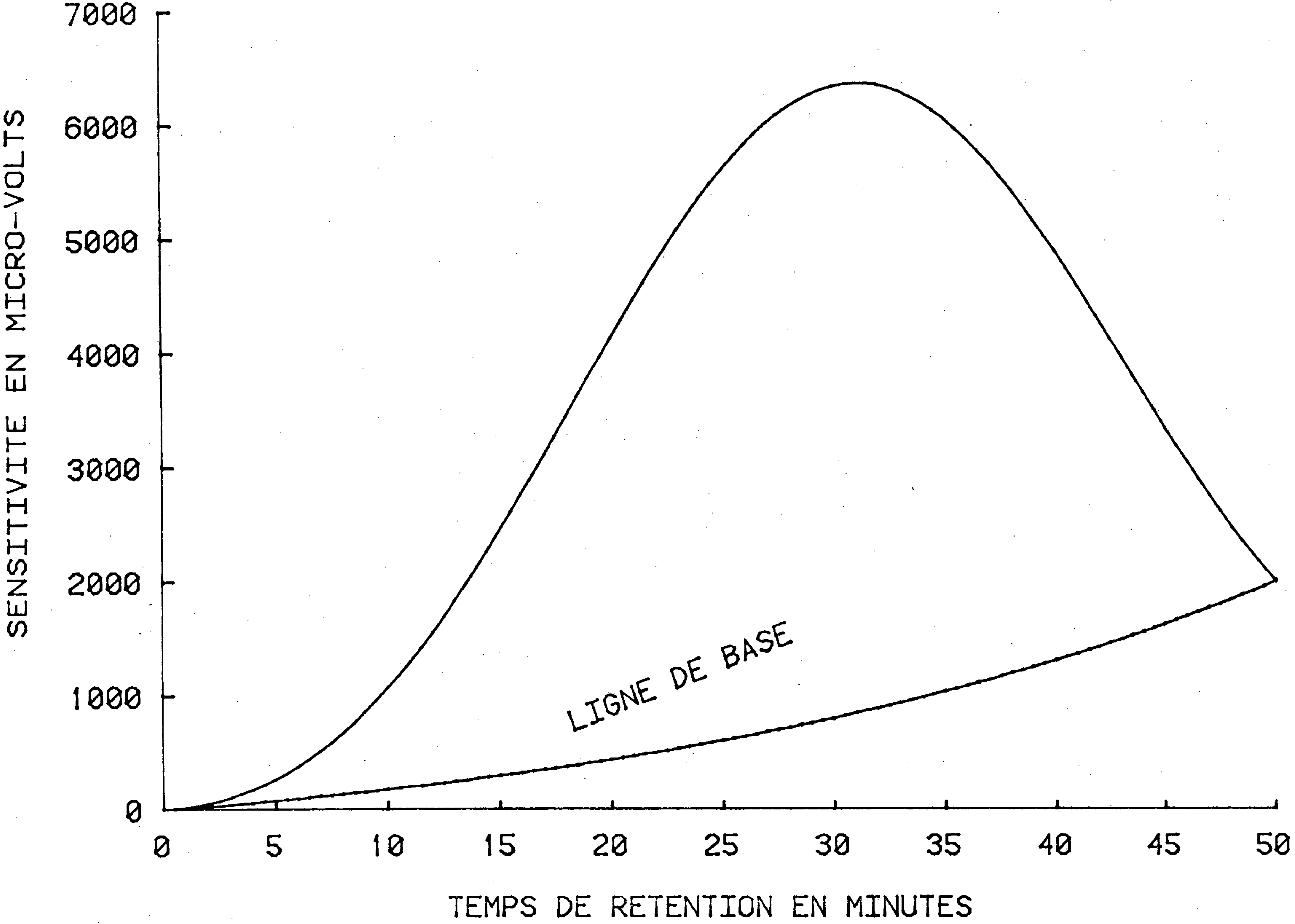
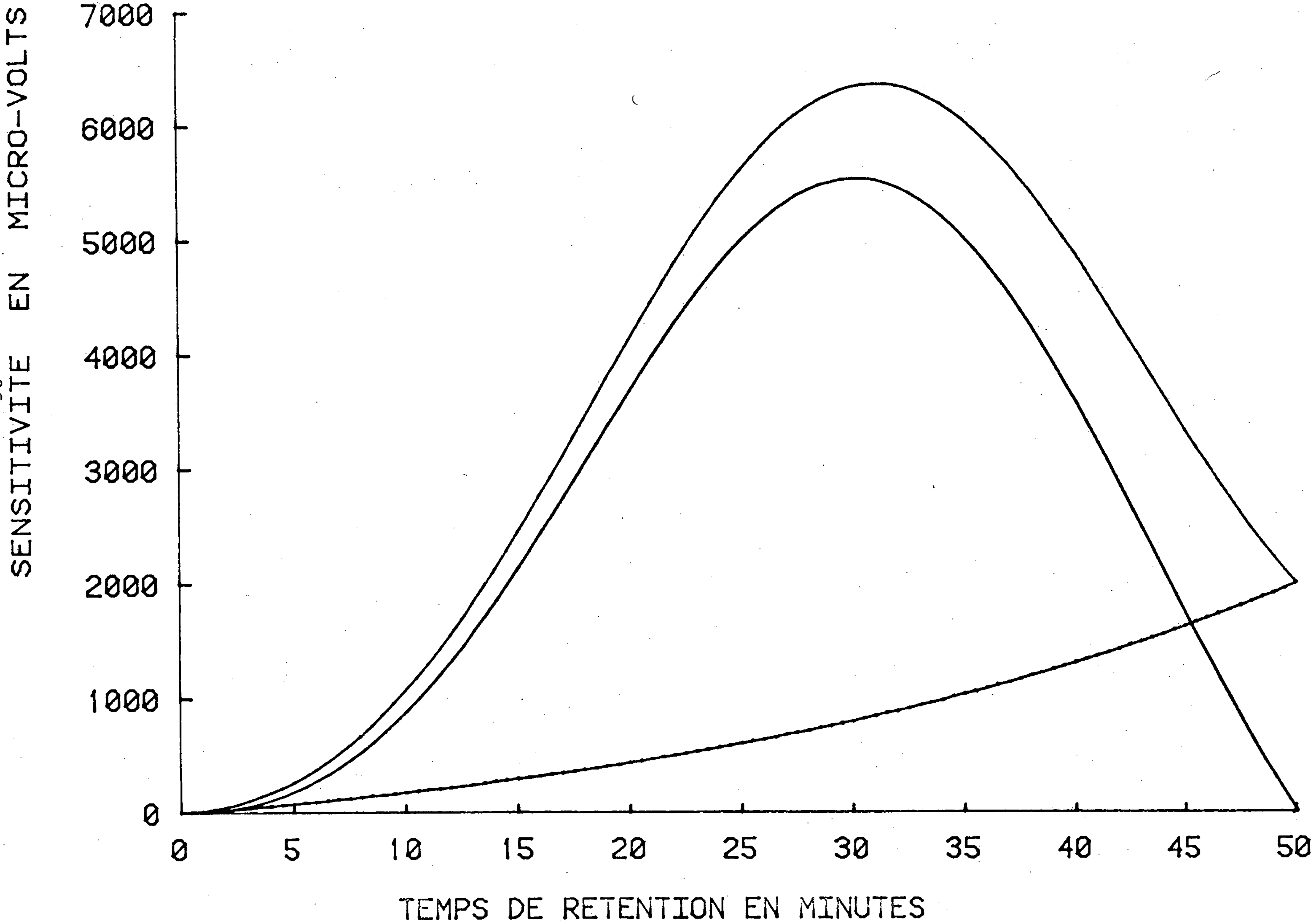
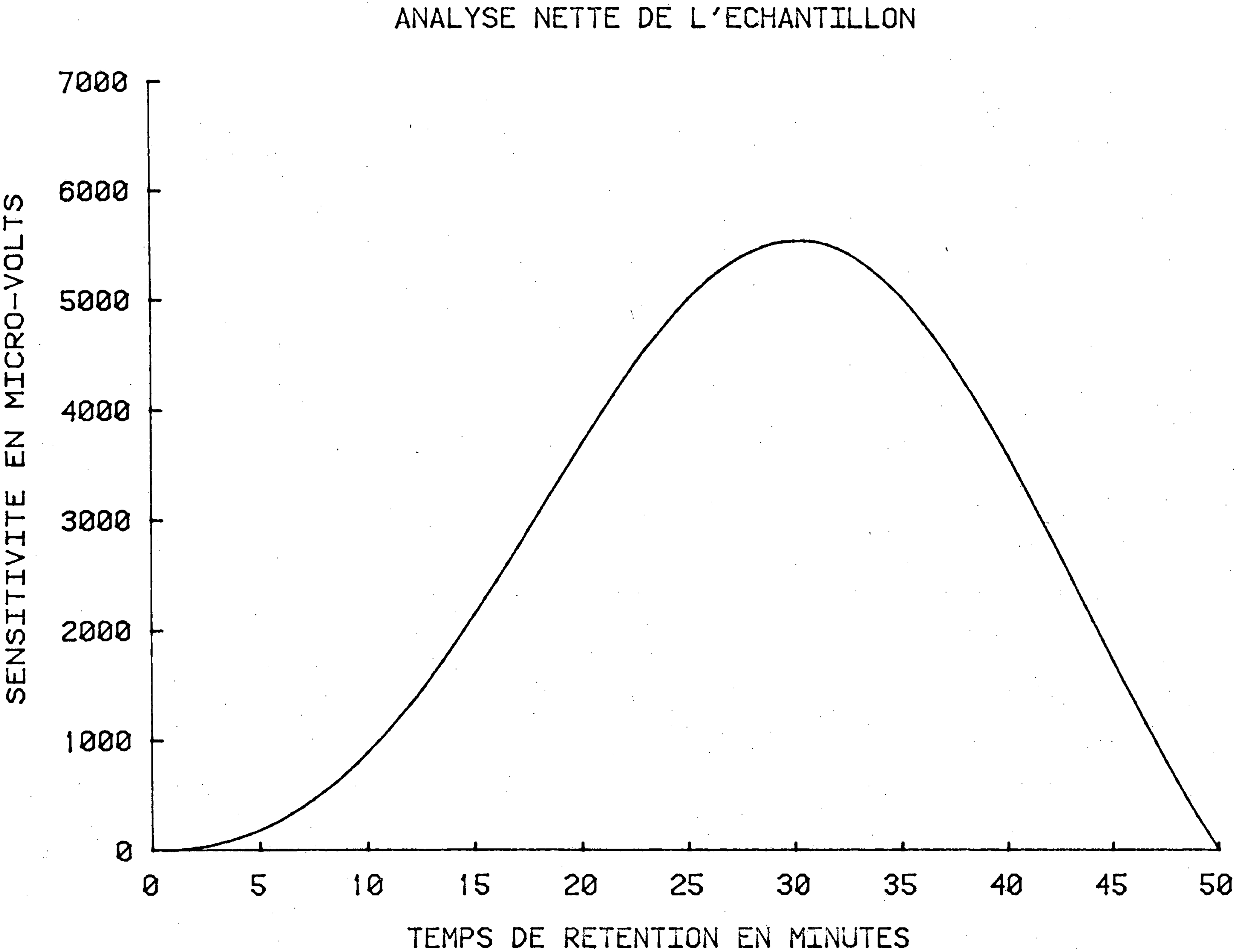

LIGNE DE BASE EN PROGRAMMATION DE TEMPERATURE
SENSITIVITE EN MICRO-VOLTS
7000
6000
5000
4000
3000
2000
1000
0
0
5
10
15
20
25
30
35
40
45
50
TEMPS DE RETENTION EN MINUTES

ANALYSE D'ECHANTILLON ET LIGNE DE BASE



SOUSTRACTION DE LA LIGNE DE BASE




ANALYSE NETTE DE L'ECHANTILLON
SENSITIVITE EN MICRO-VOLTS
7000
6000
5000
4000
3000
2000
1000
0
0
5
10
15
20
25
30
35
40
45
50
TEMPS DE RETENTION EN MINUTES

Annexe E

Contenu de la disquette "D-3710"

Méthodes:

* Calib. RT-1 : méthode avant calibration RT
* Calib. RT-2 : méthode après calibration RT
* Calib. RRF-1: méthode avant calibration RRF
* Calib. RRF-2: méthode après calibration RRF
* Analyse : méthode pour l'analyse d'échantillon.

Filière:

* ECH. 1706/000 : analyse de l'échantillon # 1706 (chromatogramme).