

4.6 Improvement of Nitrogen Content Analyzing Method for Heavy Oil by Using a Single Nitrogen Compound as Standard Substance for Calibration Curve

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Japan Petroleum Institute, September 1992

1. Introduction

In case of total nitrogen content analysis of heavy oil sample by using a Total Nitrogen Analyzer TN-05: a product of Mitubishi Petroleum Co.,

- (1) make a calibration curve with toluene solution dissolved with standard ample of heavy oil verified by the Petroleum Institute
- (2) measure the heavy oil sample dissolved with toluene, and identify the nitrogen content by using above mentioned calibration curve

it was possible to measure without any problem within the permissive error as long as following above mentioned analyzing method (1) and (2).

On the contrary, in case that a single nitrogen compound (e.g. quinoline solution in toluene solvent) is used for drawing a calibration curve, and applied to the analysis of total nitrogen content in heavy oil sample by using the TN-05, it has been widely pointed that the method tends to give a smaller nitrogen content in heavy oil than the true value.

As a result of investigation on the cause and the solution, it is concluded that the calibration method with single nitrogen compound can be used as well as the conventional method with the Standard Heavy Oil sample without any problem under the condition the method undergoes the following improvements.

2. Points of Improvement

(1) Improvement on Injection Method

This is aiming at realization of exactly same injection amount in both standard sample analysis and tested sample.

1) Conventional Method

When the injection of sample is finished, there still remains a solution of approximately 1.5 μl inside the needle of micro-syringe. At this moment, the needle of syringe has been heated by electric furnace, so that toluene and quinoline, with comparably low boiling point among those

remaining in the needle, are partly evaporated and introduced into the combustion tube of the Analyzer. On the other hand, in case of heavy oil injection, only toluene, the solvent, is partly evaporated and introduced into the combustion tube leaving heavy oil in the needle behind.

Though try to compensate the difference according to the amount of samples left in the needle, it is difficult to get an accurate value to be compensated because the concentration of the remaining solution in the needle has been changed due to unequal evaporation among the components of the solution

2) Improved Method

Suck a certain amount of toluene with micro-syringe first, suck an appropriate amount of air successively, and after that suck a sample (standard sample or tested sample), then the sample is injected into the Analyzer. As a result of this operation, the whole sample has been injected leaving only toluene behind in the needle when finished the injection. The concept of this improvement is shown in Figure 1.

(2) Improvement of Measuring Condition

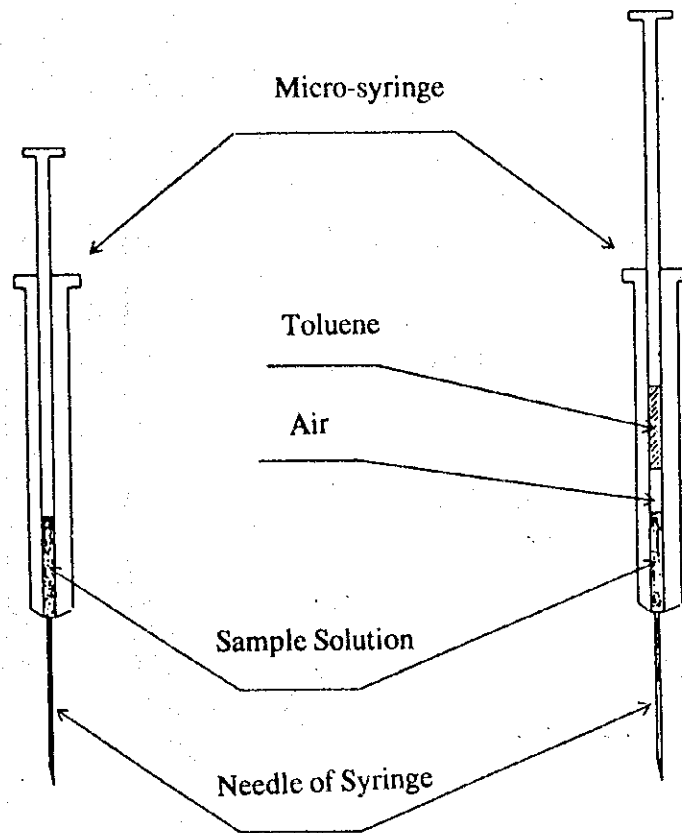
The temperature at the inlet zone (pyrolyzing zone) of combustion tube has been raised from 800 °C as conventional usage to 950 °C.

(3) Change the Shape of Internal Tube of Reactor Tube

The structure of the internal tube was modified so as to increase the contact efficiency between pyrolyzed gas and oxygen gas in argon stream. This modification effects a rise and stabilization of the conversion rate from nitrogen compound to nitrogen monoxide for any compound disregarding type and state.(refer to Figure 2)

Conventional
Method

Improved
Method



* Suck only sample solution, and inject it into the Analyzer isokinetically. When finished injection, a very little amount of the sample solution still remains in the needle and some part of the remaining sample is evaporated and introduced into the reactor tube. The amount introduced to the reactor depends on the state of the sample.

* Suck toluene, air and sample solution in this order, then inject the sample into the Analyzer. When finished injection into the reactor tube, the remnant in the needle becomes entirely toluene

Figure 1 Improvement of Sample Injection Method

Slits carved at the tip of internal tube of reactor are deepened and increased in number. As a result of this modification, the conversion rate from heavy oil to nitrogen monoxide has become equal to that from quinoline (refer to Figure 3 hereafter)

Outline of Reactor tube

Detail of Tip of Internal Tube

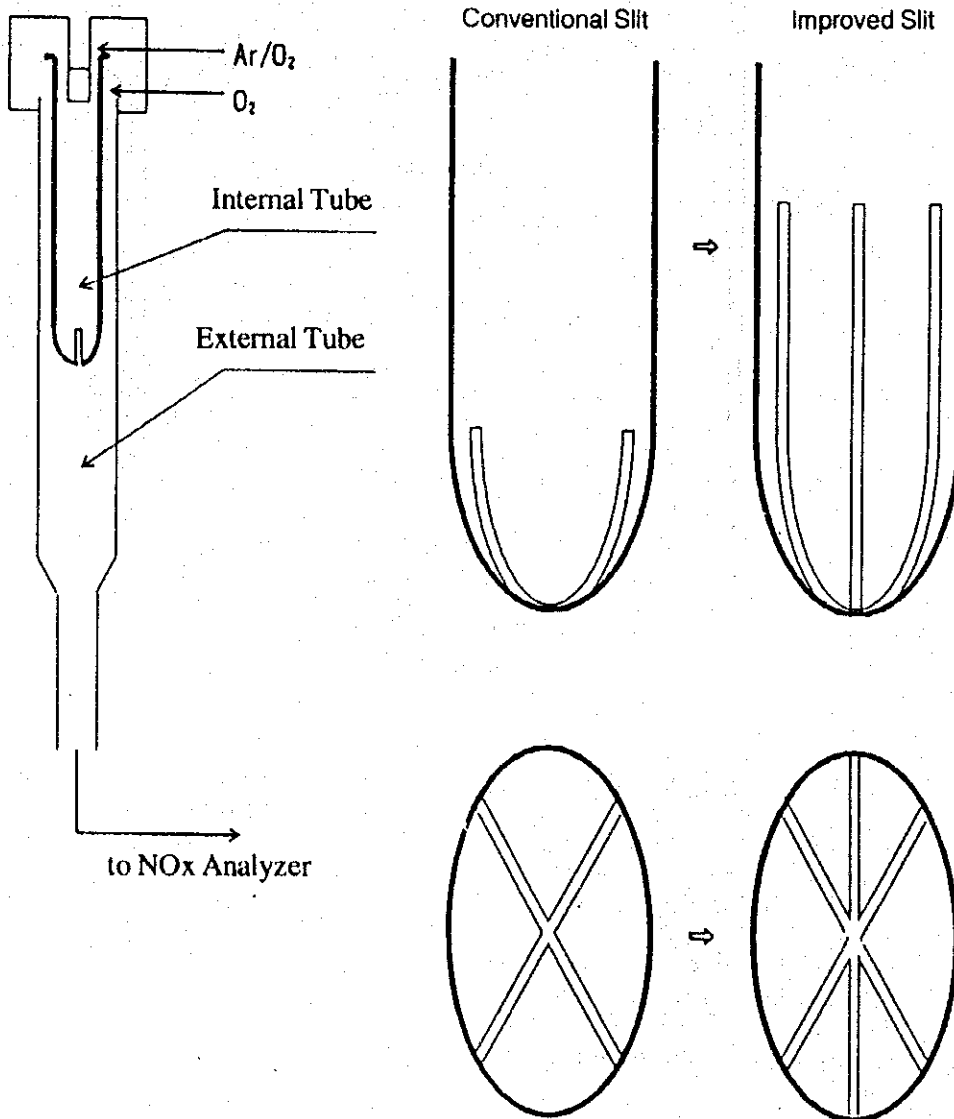


Figure 2 Modification of Reactor Tube

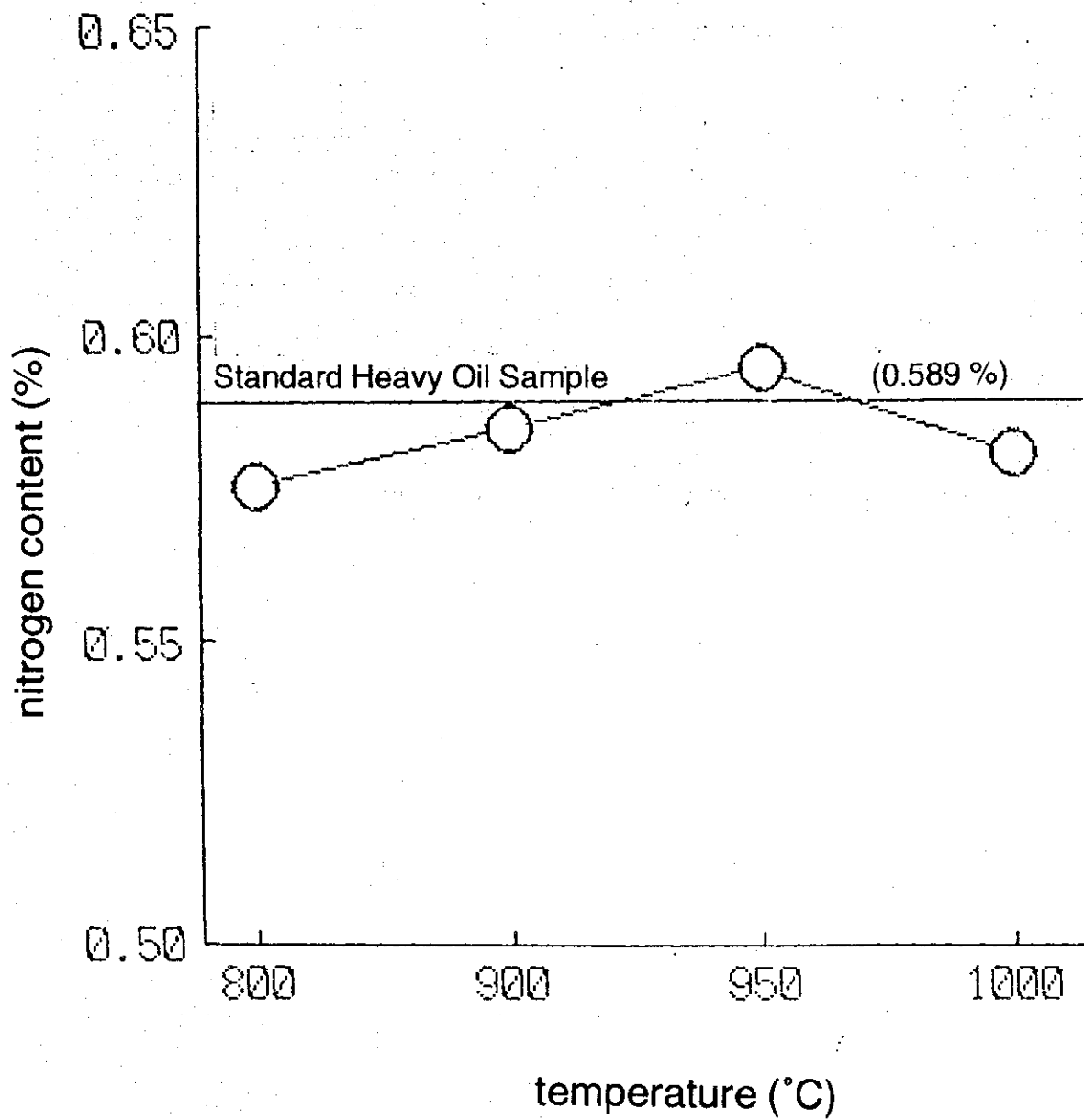


Figure 3 Evaluation of Modified Internal Tube of Reactor

3. Results of Measurement

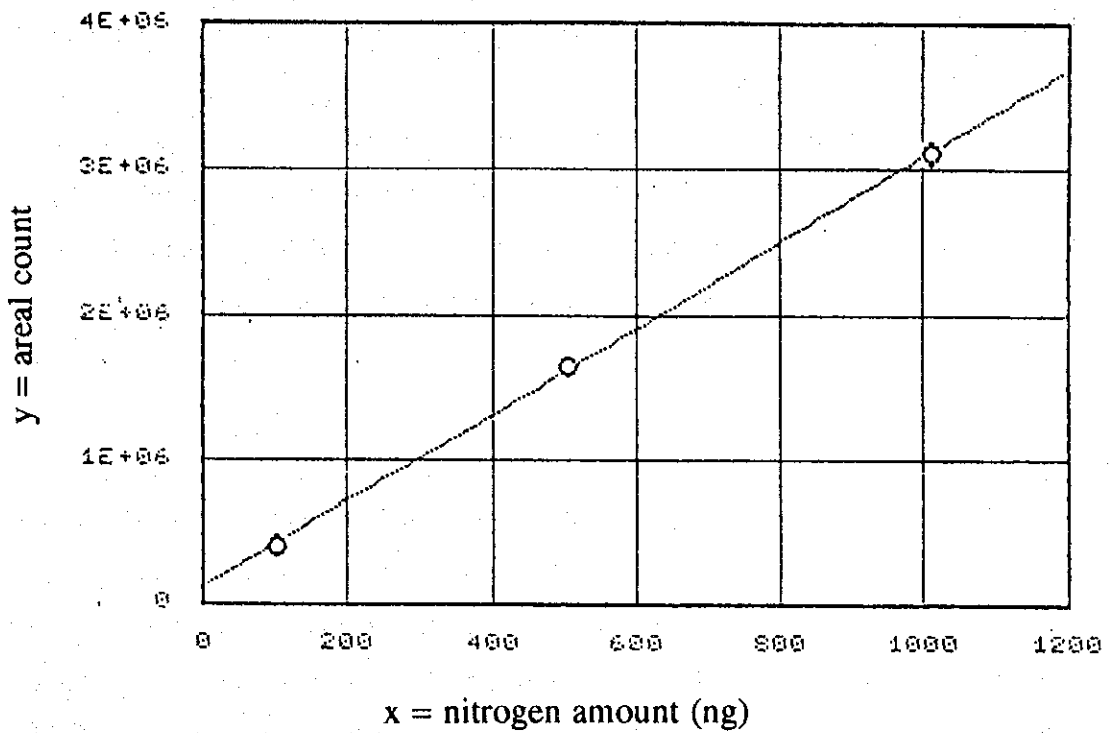
With above mentioned modifications applied, heavy oil Standard Samples verified by the Petroleum Institute were analyzed for three days according to the calibration curve created with quinoline as the standard substance. Calibration curve was composed of three points of measurement which corresponded to the concentration of quinoline in toluene solvent, 10 $\mu\text{g/ml}$, 50 $\mu\text{g/ml}$, 100 $\mu\text{g/ml}$ respectively. (refer to Figure 4) Results of the measurement are presented in the table below.

Results of Measurement of Heavy Oil Standard Sample

nitrogen content of Standard Sample (%)	1st. day			2nd. day			3rd. day		
	mean value (%)	number of data	coefficient of variation (%)	mean value (%)	number of data	coefficient of variation (%)	mean value (%)	number of data	coefficient of variation (%)
0.052	0.054	4	0.9	0.053	6	0.7	0.052	9	1
0.100	0.102	5	0.5	0.102	5	0.4	0.105	5	1
0.340	0.341	5	0.5	0.339	5	2	0.339	5	0.4
0.589	0.592	5	1	0.588	5	0.5	0.594	5	1

Note:

- (1) temperature: inlet = 950 °C, cat. = 900 °C
- (2) gas flow volume: Ar + O₂ = 0.1 l/min, O₂ = 0.6 l/min
- (3) injection amount: (sample solution) 10 μl + (toluene) 5 μl
- (4) injection speed: 1 $\mu\text{l}/\text{sec}$



Regression curve: $y = a \cdot x + b$
 $a = 2.9751946D + 03$
 $b = 1.1717666D + 05$

Figure 4 - Calibration Curve for Heavy Oil Nitrogen Content with TN-05 and Quinoline as Standard

4.7 Summary of Report of the Study on the Determination of Nitrogen in Standard Samples of Heavy Oil Nitrogen by Chemiluminescence

This committee's objective has been to improve the most commonly used chemiluminescence method so that it can substitute for the Macrokjeldahl method for determination of standard values of heavy oil nitrogen content of standards approved by the Japan Petroleum Institute. As a result, the following findings were verified for a Mitsubishi Chemical TN-05 analyzer and an Antek 7000N analyzer, and a proposal entitled "A test method for nitrogen content in heavy oil nitrogen content standards by the chemiluminescence method" was prepared.

<Mitsubishi Chemical TN-05>

1. By raising the inlet temperature of the combustion furnace to 950 °C, the rate of sample decomposition was increased.
2. Improved reaction tubes were used to facilitate heavy oil sample decomposition.
3. A micro syringe was used for sample injection thus improving reproducibility.
4. Error factors produced by sample corking were removed by changing the length of the injection needle inserted into the combustion tube and adding the sample at the lowest temperature.

<Antek 7000N>

The Antek 7000N analyzer is widely used. It is an updated model of the Dohrmann DN-10 and DN-1000 analyzers. It became the instrument of choice as a substitute for the Dohrmann's instruments after our investigation of the current state of the chemiluminescence method. The decomposition temperature was set at 1100 °C, which was the highest temperature set among all other commercially available instruments. For this reason the effect of the decomposition temperature was omitted and the following experimental conditions were identified.

1. Since the decomposition rate was different between quinoline used for standards and a heavy oil sample, the optimal analytical conditions, such as concentration range of calibration curve, sample injection volume, introduction speed of sample boat and installation of instrumental voltage and gains, were determined.

The precision and accuracy of the chemiluminescence method compared to the Macrokjeldahl method were studied on the results of the Third Joint Experiment using the test methods proposed. As a result, chemiluminescence nitrogen content experiments by the Mitsubishi Chemical TN-05 analyzer and the Antek 7000 analyzer were judged to be equivalent or better in precision in parallel experiments within one laboratory and in reproducibility between two laboratories than the Macrokjeldahl method. These conclusions are based on the analytical results of all data. In terms of accuracy, "no difference was found" at the 0.30 weight % level, but "differences were found" at other concentration levels (0.05, 0.10, 0.50 weight %). These differences were analyzed statistically and the difference between t-test values and the average value at all concentrations was smaller than the tolerance of the joint experiments. Since the deviation varied randomly, either higher or lower according to the concentration levels of nitrogen, we concluded that there was no difference between the chemiluminescence and the Macrokjeldahl method.

Based on the results mentioned above, the chemiluminescence method provides experimental precision and accuracy sufficient to substitute for the Macrokjeldahl method for determination of standard values of heavy oil nitrogen content in standards.

Committee members suggest keeping the following points in mind when making a decision on whether Committee of Standards will adopt or reject the chemiluminescence method as a substitute for the Macrokjeldahl method.

- (1) The method is different from the Macrokjeldahl method (the absolute method). Since the chemiluminescence method is a comparative analytical method, it is essential to set up an instrument which provides accuracy; the instrument should be under optimal conditions when used as a substitute, and before measurement, one must identify that the nitrogen recovery is more than 97% using a lot (a heavy oil nitrogen content standard) which has a same level of nitrogen concentration as the heavy oil nitrogen content standard used for a determination of standard nitrogen.
- (2) If a question is raised in the use of this method, the determination by the Macrokjeldahl method as an absolute method may be required. Therefore, for the current state of experimental and analytical systems used by each organization, it is

desirable to maintain the level of experimental technology among the participants of Petroleum organizations since the Macrokjeldahl method is considered to be a basic method for the investigation of nitrogen content in Petroleum although it is not used daily.

- (3) In use of the Macrokjeldahl method for the determination of standard values of standard compounds, if the number of participating organizations is too small, one can either send a sample to outside organizations or utilize both the chemiluminescence and Macrokjeldahl methods for comparison. One can maintain the technology level by keeping the organizations which utilize the Macrokjeldahl method among the Petroleum related organizations.

June 6, 1994

Committee Specializing in Nitrogen Analysis

A test method for nitrogen content in heavy oil nitrogen content standards by chemiluminescence (Proposal)

1. Scope of Application

This proposal describes a method to determine nitrogen content in heavy oil nitrogen content standards.

2. Abstract of Test Method

After sample is injected into the combustion tubes heated at a high temperature, the sample is decomposed and oxidized in the presence of oxygen. Nitrogen compounds in the sample are converted into nitrogen monoxide. Then, by reacting with ozone, nitrogen monoxide is converted into nitrogen dioxide being at an excited state. By detecting luminescence using a photomultiplier tube, which occurs when nitrogen dioxide at an excited state returns to the ground state, nitrogen content is determined.

3. Analyzers

Chemiluminescence analyzers, the Antek 7000N and the Mitsubishi Chemical TN-05, both of which are certified by JIS K 2609 7.2. The improved model should be used for the Mitsubishi Chemical TN-05 attached with reaction internal tubes for heavy oil.

4. Reagents

Reagents for the chemiluminescence method are:

1) Oxygen

One defined by JIS K 1101

2) Inert gas

Argon or helium whose purity exceeds 99.998 volume %

3) Drying agents (Magnesium perchlorate)

One defined by JIS K 8228

4) Quinoline, C_9H_7N , MW 129.15, 10.845 weight %N

One defined by JIS K 8279

5) Toluene

One defined by JIS K 8680

6) Nitrogen standard solution

Quinoline solution ($1000 \mu\text{g N/ml}$) is prepared as follows;

Quinoline 0.920 g (weight to the third decimal place) is mixed with toluene to make a 100 ml solution in a volumetric flask. The concentration of nitrogen in this solution is found using the following equation and is rounded off as defined by JIS K 8401;

$$A = 10.845 Q \times 100,$$

where A is a nitrogen concentration of the quinoline solution ($\mu\text{g N/ml}$), Q is a weighted amount of quinoline (g), and 10.845 is nitrogen content of quinoline (weight volume %).

7) The concentration of the standard quinoline solution for calibration ($100 \mu\text{g N/ml}$) is prepared as follows;

Take 10 ml of the standard quinoline solution ($1000 \mu\text{g N/ml}$) with a pipette and dilute into 100 ml with toluene. The concentration of nitrogen for this solution is $A/10$, and is rounded off at the first decimal place as defined by JIS K8401.

8) The concentration of the standard quinoline solution for calibration ($50 \mu\text{g N/ml}$) is prepared as follows;

Take 5 ml of the standard quinoline solution ($1000 \mu\text{g N/ml}$) with a pipette and dilute into 100 ml with toluene. The concentration of nitrogen for this solution is $A/20$, and is rounded off at the first decimal place as defined by JIS K8401.

5. Preparation of Analyzer

Preparation of the analyzers for the chemiluminescence method is as follows;

(1) Setting of test conditions

Set a gas flow, a temperature of combustion burner, initial conditions of detectors and injection conditions of the sample. An example of test conditions is shown in Table 1.

Table 1 Parameters of Measurement

Item		Antek 7000 N	Mitsubishi Chemical TN-05
Flow of oxygen (ml/min.)	Carrier, reaction-internal tube	Approx. 20 (0.6)	Approx. 100
	Reaction tube	Approx. 480 (4.0)	Approx. 600
	Ozonator	Approx. 40 (1.6)	Approx. 60
Flow of inert gas (ml/min.)	Carrier, reaction-internal tube	Approx. 150 (3.5)	Approx. 100
	Purge	Approx. 100	
Time for changeover of gas (sec.)	Argon		30
	Oxygen		120
Temperature in combustion furnace (°C)		Approx. 1,100	Part of injection : Approx. 950 Part of catalyst : Approx. 900
Detector	PMT voltage (V)	600~700	
	Gain, factor	Hi, x 10	
	Range (ppm)		10
	Monitoring time at peak (min.)	Approx. 3.5-4.0	
Part of sample injection	Volume of syringe (μℓ)	10	10 (25)
	Volume of sample injection (μℓ)	5	10 (10)
	C-vol		10
	Insertion speed (mm/min.)	Approx. 180(750)	
	Injection speed (mm/min.)		1.0(4.0)

Note 1: Gas flow of the Antek 7000N and a sample injection port:

Figures in parentheses represent the marked graduation values of a flow meter and of a fixed injection drive of the analyzer.

Note 2: Sampling speed of the Mitsubishi Chemical TN-05:

The figures represent the speed in case of using an automatic sample changer (ASC-11). Figures in parentheses represent the set-up values (the marked graduation values of the analyzer) in case of using a constant injector (CRI).

Note 3: Automatic sample changer (ASC-11) of the Mitsubishi Chemical TN-05:

The position of sample injection by a sample injection needle (the insertion depth in the combustion tube).

Loose two screws at the lower portion of the right side of an adjustable needle holder and adjust a limit slit to the top position and tighten the screws.

(2) Preparation for Calibration Curve

Generate a calibration curve (a primary equation) with a nitrogen standard solution for each analyzer.

1) Calibration curve for the Antek 7000N

i) In case of using a multi-matrix inlet / a Model 735 fixed injection drive

- a) Take 5 $\mu\ell$ of the quinoline solution (100 $\mu\text{g N}/\text{m}\ell$) used for a calibration curve accurately with a 10 $\mu\ell$ micro syringe. Insert a needle tip of micro syringe into the sample injection port of multi-matrix inlet to inject the solution into a sample boat, then start measurement by turning a start-switch on.
- b) Repeat the operation of (a) three times. Calculate the average from each peak area and generate a calibration curve starting from the origin (the zero peak area) to the average. However, if error exceeds 5%, repeat the measurement.

Reference: An accurate reading of the injected volume of the quinoline solution for calibration can be found from the difference of readings by sucking the same volume of air into the syringe before and after filling with a fixed volume of the solution.

ii) In case of using an automatic sampler

- a) Set the volume of sample injection of the automatic sampler at 5 $\mu\ell$. Inject the quinoline solution (100 $\mu\text{g N}/\text{m}\ell$) used for a calibration curve into a several designated vials and put the caps attached with septa on. Set the vials in the automatic sampler.
- b) Set the repeating time at 3 and start measurement. Calculate the average from each peak area and generate a calibration curve between the origin (the zero peak area) and the average.

Note: The measurement and calculation are conducted automatically and a calibration curve is generated.

2) A calibration curve for the Mitsubishi Chemical TN-05

i) In case of using a constant injector (CRI)

- a) Suck 5-10 $\mu\ell$ of toluene with a 25 $\mu\ell$ micro syringe, first. After sucking an appropriate volume of air (1-2 $\mu\ell$), take 10 $\mu\ell$ of the quinoline solution (50 $\mu\text{g N}/\text{m}\ell$) used for a calibration curve accurately, set it on the CRI and inject it. After the injection, turn the syringe support to the left, shake the syringe up and down once or twice to drop a remaining solution on the needle tip into the reaction tube. Once the measurement is started, the peak area is calculated

automatically.

b) Repeat the operation of (a) three times. Calculate the average from each peak area and generate a calibration curve between the origin (zero peak area) and the measured peak areas.

ii) In case of using an automatic sample changer (ASC-11)

a) Inject the quinoline solution ($100 \mu\text{g N/ml}$) used for a calibration curve into a several designated vials and put the cap attached with septa on. Set the vials at the designated positions.

b) Set the repeating time at 3 and start measurement. Calculate the average from each peak area and generate a calibration curve between the origin (the zero peak area) and the average.

Note: The measurement and calculation are conducted automatically, and a calibration curve is generated.

6. Sampling Method for Heavy Oil Standards

After shaking sampling bottles vigorously to make a homogeneous sample, weight out the sample. Heat at $40-50 \text{ }^\circ\text{C}$ in advance for a highly viscous sample which has a low fluidity at a normal temperature.

7. Measurement of Heavy Oil Standards

Referring to Table 2, weigh a sample accurately to the third decimal place and store it in the volumetric flask. Dilute with toluene so that the final concentration of nitrogen becomes similar to the concentration of nitrogen of standard solutions prepared in 5.(2). This is used as a sample solution. Analyze in the same way as described in 5.(2) to find the concentration of nitrogen.

Table 2 Amount of sample weighted and Volume of Flask by the Level of N Content in Sample

N content level in sample (wt. %)	Antek 7000 N		Mitsubishi Chemical TN-05	
	Amount of sample weighted (g)	Volume of flask (ml)	Amount of sample weighted (g)	Volume of flask (ml)
0.05	Approx. 4.0	20	Approx. 2.0	20
0.1	Approx. 2.0	20	Approx. 2.5	50
0.3	Approx. 1.7	50	Approx. 1.7	100
0.5	Approx. 1.0	50	Approx. 1.0	100

8. Calculation and Results

Nitrogen content measured with the chemiluminescence method is calculated by the following equation, and is rounded off to the third decimal place as described in JIS Z 8401.

$$TN = \frac{N \cdot V}{M} \times 0.0001$$

where

TN: Nitrogen content in sample (wt.%)

N: Concentration of nitrogen ($\mu\text{g N/ml}$)

V: Volume of volumetric flask (ml)

M: Amount of sample weighted (g)

9. Repeating Test

Prepare the quinoline solution used for a calibration curve as described in the procedure 4.(7) or 4.(8). The second measurement should be conducted on a different day or time, following the direction as described 5. to 8.

Note: After the second measurement, if the difference between the two results exceeds the tolerance, prepare a fresh quinoline solution used for a calibration curve as described in the procedure 4. (7) or 4. (8) and repeat again, following the direction as described 5. to 9.

10. Precision of Test

The precision of the chemiluminescence method is as follows;

(1) The precision in parallel experiments within one laboratory

The difference of the results should not exceed the tolerance shown in Table 3, if the same person in the same laboratory using the same sample with the same analyzer repeats the measurement twice and the two results are compared.

(2) The Precision of reproducibility between two laboratories

The difference of the results should not exceed the tolerance shown in Table 3, if two different persons in two different laboratories using the same solution with two different analyzers do the measurement once and the results are compared.

Table 3 The Precision of Test (wt. %)

Nitrogen content	Tolerance in parallel within one laboratory	Tolerance of reproducibility between two laboratories
0.01 or more - 0.10 or less	0.01	0.02
More than 0.10 - 0.20 or less	0.01	0.04
More than 0.20	0.02	0.06

Appendix 1. Citation of Standards

JIS K2251: Sampling Method of Crude Oil and Petroleum

JIS K 2839: Glassware for Testing Petroleum

JIS K8279: Quinoline

JIS K 8680: Toluene

JIS Z 8401: Method of Rounding Off

JIS Z 8402: General Rules for Tolerance of Analysis and Test

Appendix 2. Source

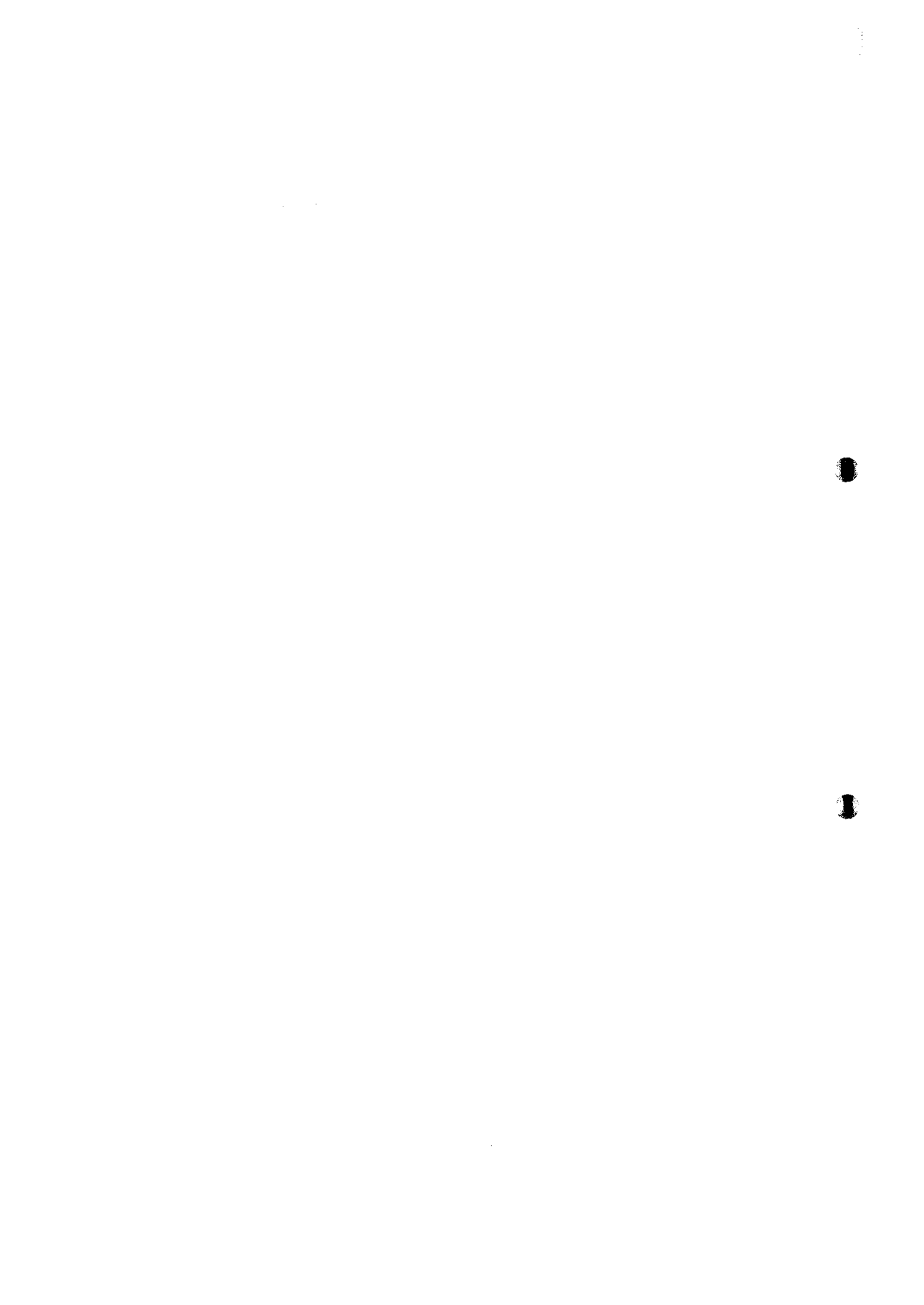
Report on the Results of Nitrogen Content Test Method of Heavy Oil Nitrogen Content Standards by the Chemiluminescence Method

March 1995

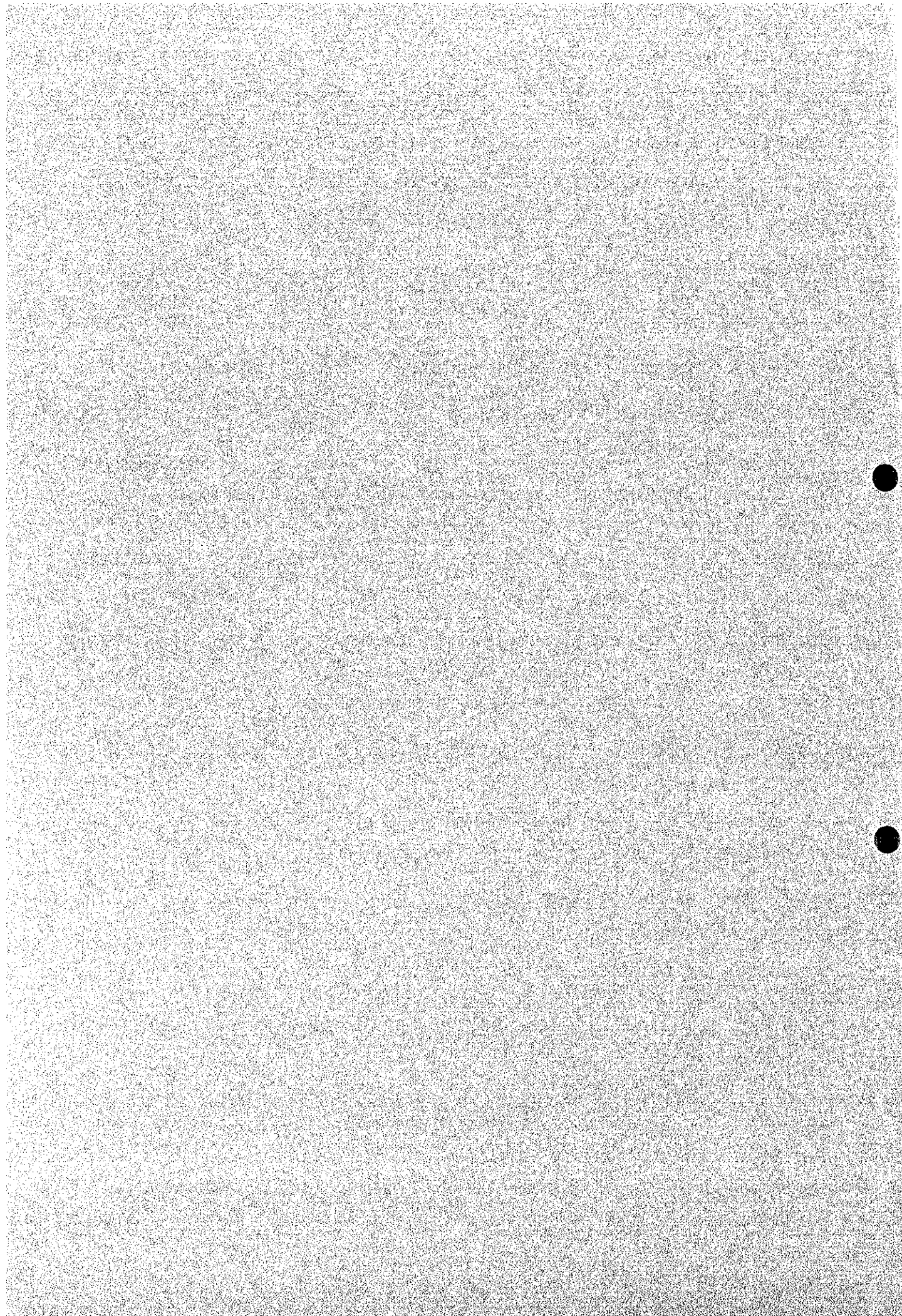
The Japan Petroleum Institute

Products Division Test and Analysis Section

Committee Specializing in Nitrogen Analysis



REFERENCES



References

A. POLLUTION CONTROL PLAN

- A1 PROGRAMA INTEGRAL CONTRA LA CONTAMINACION ATMOSFERICA EN LA ZONA METROPOLITANA DE LA CIUDAD DE MEXICO (PICCA), "Un Compromiso Común," METROCOM, October 1990.
- A2 PROGRAMA PARA EL CONTROL DE EMISIONES CONTAMINANTES AL AIRE PRVENIENTES DE LA INDUSTRIA EN LA ZONA METROPOLITANA DE LA CIUDAD DE MEXICO, METROCOM, March 24, 1992.
- A3 PICCA, "AVANCES A SEPTIEMBRE DE 1992," METROCOM.
- A4 PICCA, "AVANCES A DICIEMBRE DE 1992," METROCOM.
- A5 PICCA, "AVANCES A SEPTIEMBRE DE 1993, METROCOM.
- A6 PICCA, "MEDIDAS DE INVIERNO 1992-1993," METROCOM, April 15, 1993.
- A7 PICCA, "MEDIDAS DE INVIERNO 1993 - 1994," METROCOM, May 9, 1994.
- A8 PICCA, "PROGRAMA DE CONTROL DE EMISIONES CONTAMINANTES AL AIRE PRVENIENTES DE LA INDUSTRIA EN LA ZONA METROPOLITANA DE LA CIUDAD DE MEXICO, AVANCES (BORRADOR)," METROCOM, November 1993.
- A9 OZONO, BASES PARA LA ELABORACION DE UNA ESTRATEGIA DE CONTROL, METROCOM, November 24, 1992.
- A10 The Study on the Air Pollution Control Plan of Stationary Sources in the Metropolitan Area of the City of Mexico, Final Report, JICA, September 1991.

B. EMISSIONS, EMISSION CONTROL AND STANDARDS

- B1 Control of Atmospheric Emissions From Service Facilities in the Mexico City Metropolitan Area, Final Report, Canadian International Development Agency, Industrial Cooperation Division, February 1992.
- B2 List of Emission Sources Registered by INE, February 1994.
- B3 NORMA OFICIAL MEXICANA, NOM-085-ECOL-1994, CONTAMINACION ATMOSFERICA - FUENTES FIJAS -, DIARIO OFICIAL DE LA FEDERACION, December 2, 1994.

- B4 NORNAS OFICIALES MEXICANAS, NOM-PA-CCAT-019-93, NOM-PA-CCAT-022-93, NOM-PA-CCAT-023-93, DIARIO OFICIAL DE LA FEDERACION, April 7, 1993.
- B5 PROYECTOS DE NORMAS OFICIALES MEXICANAS, NOM-PA-CCAT-001/93, NOM-PA-CCAT-002/93, NOM-PA-CCAT-005/93, NOM-PA-CCAT-006/93, NOM-PA-CCAT-009/93, NOM-PA-CCAT-015/93 (Proposed emission standards for stationary sources), DIARIO OFICIAL DE LA FEDERACION, June 23, 1993.
- B6 NORMA OFICIAL MEXICANA, NOM-CCAT-019-ECOL/1993 (NE) (preceding emission standards for boilers), DIARIO OFICIAL, November 18, 1993.
- B7 NORMA OFICIAL MEXICANA, NOM-086-ECOL-1994 (requirements on quality of liquid and gaseous fossil fuels), DIARIO OFICIAL, December 2, 1994.
- B8 PROYECTO DE NORMA OFICIAL MEXICANA, NOM-097-ECOL-1994 (emission standards for glass factory), DIARIO OFICIAL, December 2, 1994.
- B9 Technologies, Laws and Regulations for Pollution Control, Japan Environmental Management Association for Industry, 1994.
- B10 Manual of Practice for Boilers and Pressure Vessels, Japan Boiler Association, Osaka Branch, November 1978.
- B11 Manual for Nitrogen Oxides Emission Reduction Technology, Tokyo Metropolitan Government, Environment Protection Bureau, 1984.
- B12 PPM Monthly Journal, April 1979, Japan Industrial Newspaper, Co.

C. AMBIENT AIR QUALITY AND STANDARDS

- C1 REPORTE ANUAL SOBRE LA CALIDAD DEL AIRE EN LA CIUDAD DE MEXICO, DDF, January 1992.
- C2 INFORME MENSUAL DE LA CALIDAD DEL AIRE, DDF, April - September 1993.
- C3 CALIDAD DEL AIRE EN LA CIUDAD DE MEXICO: RESULTADOS DE INVESTIGACION APLICADA CON PARTICIPACION INTERNACIONAL, Alcérreca, V. M. and Guzmán, F., IMP, December 10, 1993.
- C4 RED DE MONITOREO ATMOSFERICO DE LA ZONA METROPOLITANA DE LA CIUDAD DE MEXICO, INFORME MENSUAL DE LA CALIDAD DE AIRE, METROCOM, September 1993.

- C5 RED DE MONITOREO ATMOSFERICO DE LA ZONA METROPOLITANA DE LA CIUDAD DE MEXICO, INFORME MENSUAL DE LA CALIDAD DE AIRE, METROCOM, December 1993.
- C6 Air Pollution in Mexico City, Present Situation, METROCOM, May 1994.
- C7 PROYECTOS DE NORMAS OFICIALES MEXICANAS, NOM-020-SSA1-1993 (O₃), NOM-021-SSA1-1993 (CO), NOM-022-SSA1-1993 (SO₂), NOM-023-SSA1-1993 (NO₂), NOM-024-SSA1-1993 (TSP), NOM-025-SSA1-1993 (PM10), NOM-026-SSA1-1993 (Pb), DIARIO OFICIAL DE FEDERACION, January 18, 1994.

D. ENERGY

- D1 BALANCE NACIONAL ENERGIA 1992, SEMIP.
- D2 AUDITORIA ENERGETICA, BA OS LUPITA, CIEDAC under the contract of DDF, August 1992.
- D3 INFORME 1990 - 1994, CONAE, November 3, 1994.
- D4 PABRAS DE INAUGURACION, CONFERENCIA DE EFICIENCIA ENERGETICA EN AMERICA LATINA: OPORTUNIDADES Y PERSPECTIVAS REGIONALES, Alfredo Elias Ayub, Subsecretary of Hydrocarbon, General Direction of Hydrocarbon Policy, SEMIP, March 23, 1994.
- D5 RAROP Heavy Oil Processing Handbook, Research Association for Residual Oil Processing, Tokyo, April 1991.
- D6 H-OIL PROCESS, IMP, SGTI, DIV. DE CONTROL ENERGETICO.
- D7 Study on Energy Saving Plan for Hungary, Report (II), Japan International Cooperation Agency, 1993.
- D8 Judgement Criteria for Rationalization of Energy Utilization in Factories, Notification of Ministry of International Trade and Industry, Japan, No.388 September 1993.
- D9 Monthly Journal of Energy Saving, Vol. 38, No.4, 1986, Japan Energy Saving Center.

E. MEASUREMENTS AND LABORATORY

- E1 LEY FEDERAL SOBRE METROLOGIA Y NORMALIZACION, DIARIO OFICIAL DE LA FEDERACION, July 1, 1992.
- E2 SISTEMA NACIONAL DE ACREDITAMIENTO DE LABORATORIOS DE PRUEBAS, SERIE NORMAS, SECOFI.

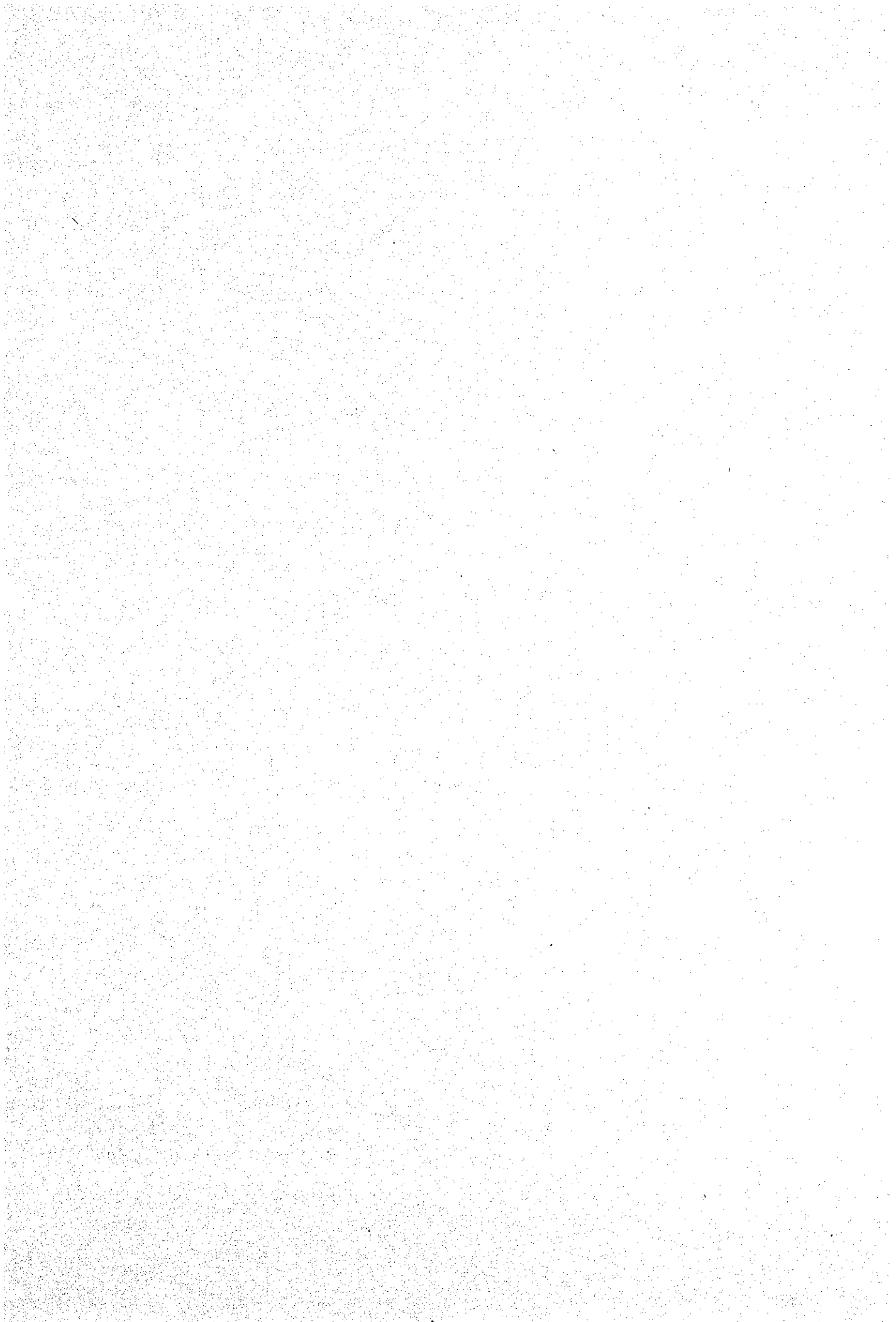
- E3 NORMA OFICIAL MEXICANA NMX-CC 13, CRITERIOS GENERALES PARA EL FUNCIONAMIENTO DE LOS LABORATORIOS DE PRUEBAAS, DIRECCION GENERAL DE NORMAS, SECOFI
- E4 LISTADO DE LABORATORIOS ACREDITADOS ANTE EL SISTEMA NACIONAL DE ACREDITAMIENTO DE LABORATORIOS DE PRUEBA, SINALP, January 1994.
- E5 List of Monitoring Service Company Registered by INE, February 15, 1994.
- E6 Improvement of Nitrogen Content Analyzing Method for Heavy Oil by Using a Single Nitrogen Compound as Standard Substance for Calibration Curve, Japan Petroleum Institute, September 1992.
- E7 Report of the Study on the Determination of Nitrogen in Standard Samples of Heavy Oil Nitrogen by Chemiluminescence, Expert Committee for Nitrogen Analysis, Japan Petroleum Institute, March 1995.

F. SOCIO-ECONOMY

- F1 Mexican Bulletin of Statistical Information, Number 11 January - March, 1994.
- F2 X CENSO COMERCIAL, RESULTADOS DEFINITIVOS, CENSOS ECONOMICOS, 1989.
- F3 XIII CENSO INDUSTRIAL, RESULTADOS DEFINITIVOS, RESUMEN GENERAL, CENSOS ECONOMICOS, 1989.
- F4 XI CENSO GENERAL DE POBLACION Y VIVIENDA, 1990, INEGI.

G. OTHERS

- G1 REGULAMENTO PARA LA INSPECCION DE GENERADORES DE VAPOR Y RECIPIENTES SUJETOS A PRESION, DIARIO OFICIAL DE LA FEDELACION, October 25, 1954
- G2 CAPACITACION EN TECNOLOGIA DE VANGUARDIA CON TECNOLOGIA DE VANGUARDIA, DESARROLLO PROFESIONAL EN TECNOLOGIA AVANZADA, A.C., November 1992



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