



ADVANCED ANALYSIS TECHNOLOGY FOR MOX FUEL

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Abstract

PNC has developed MOX fuels for advanced thermal reactor (ATR) and fast breeder reactor (FBR). The MOX samples have been chemically analysed to characterize the MOX fuel for JOYO, MONJU, FUGEN and so on. The analysis of the MOX samples in glove box has required complicated and highly skilled operations. Therefore, for quality control analysis of the MOX fuel in a fabrication plant, simple, rapid and accurate analysis methods are necessary. To solve the above problems, we have developed instrumental analysis and techniques. This paper describes some of the recent developments in PNC.

2. Outline of recently developed analysis methods by PNC.

2.1 Determination of oxygen to metal atomic ratio (O/M) in MOX by non-dispersive infrared spectrophotometry (NDIR) after inert gas fusion. The sample and nickel metal flux were fused in a graphite crucible using an impulse furnace under a helium atmosphere. The oxygen in the MOX fuel was quantitatively reacted with the carbon in the graphite crucible and carbon monoxide was evolved, which was determined using the NDIR. The oxygen content in the MOX and the O/M were calculated from the carbon monoxide analysis results. The relative standard deviations (RSD) were less than 0.35% for the MOX pellets of 5% and 25% plutonium. The time required for one determination was about 10 minutes. The apparatus was originally developed in collaboration with PNC and Horiba Co. Ltd.

2.2. Determination of occluded gas component analysis in MOX using gas sampling unit and gas chromatography. The gases extracted from the sample at vacuum condition were injected into a gas chromatograph through an originally developed gas sampling unit. The gases were simultaneously determined using the improved gas chromatograph equipped with several separation columns and a photo-ionization detector. The RSD were 1.0, 3.4, 0.6, 1.0, 1.4, 0.8 and 0.9% for H₂, O₂, N₂, CH₄, CO₂, CO and C₂H₆, respectively. The results of gas analysis using this method agreed with the high temperature vacuum extraction method in the range of less than 300 μ l of extracted gas.

2.3. Determination of nitrogen in MOX by gas chromatography after inert gas fusion. This technique is based on chromatographic determination of nitrogen in released gases from fused sample. The sample and iron metal flux in a graphite crucible were heated up to 2700 μ C under a helium atmosphere. From the fused sample, which were gases evolved such as hydrogen, nitrogen and a large amount of carbon monoxide. The carbon monoxide produced was interfered with the measurement of nitrogen. Therefore the aim of nitrogen separation was determined using a thermal conductivity detector. The RSD was less than 5%, and the time required for one determination was about only 10 minutes.

3. Future Plans. In order to put these analysis technologies for MOX to practical use, further improvements are needed. Particularly, the development of automatic handling systems, simultaneous determination methods for impurity and more accurate methods need to be developed.

1. INTRODUCTION

PNC has developed MOX fuels for advanced thermal reactor (ATR) and fast breeder reactor (FBR). The MOX samples have been chemically analysed to characterize the MOX fuel for JOYO, MONJU, FUGEN and so on. The analysis of the MOX samples in glove box has required to complicated and high skilled operations. Therefore, for quality control analysis of the MOX fuel in a fabrication plant, simple, rapid and accurate analysis methods are essential. To solve the above problems, we have developed instrumental analysis and techniques. This paper describes some of the recent developments in PNC.

2. DETERMINATION OF OXYGEN TO METAL ATOMIC RATIO IN MOX BY NONDISPERSIVE INFRARED SPECTROPHOTOMETRY AFTER INERT GAS FUSION

The present method is based on the extraction gas analysis using nondispersive infrared spectrophotometry (NDIR) after inert gas fusion. The oxygen in the fused sample was quantitatively reacted with the carbon in a graphite crucible and the CO generated was determined using the NDIR. The relative standard deviation (RSD) was less than 0.20%, and the time required for one determination was about 10 min for all analytical operations. This method is applicable to sintered MOX fuels over a wide range of plutonium content.

2.1 EXPERIMENTAL

2.1.1 The O/M analysis apparatus

The O/M analysis apparatus consists of a gas extraction unit, a gas dilution unit, the NDIR, an operating controller, and a computerized peak-area integrator. The schematic diagram of the apparatus is shown in Fig. 1. The gas extraction unit consists of an impulse furnace, a power supply, a refrigerator and a compressor. The impulse furnace consists of the upper and lower electrodes and the electrode driving cylinder. The heating conditions of the sample were controlled using the operating controller. The gas dilution unit consisted of a dilution vessel, a pressure regulator and a needle valve. The gas extracted from the fused sample was divided into 2 and 8 by the gas dilution unit. This is the reason why the NDIR that utilized linear response range for carbon monoxide determination is designed and constructed. A computerized peak-area integrator from Shimazu Co., Ltd. (Kyoto, Japan) CR-3A was used.

2.1.2 Measurement Procedure

The sample (ca. 20 - 50mg) was packed into a nickel capsule and weighed to an accuracy of 0.1mg. The inlet of the capsule was sealed off using a manual type press with a pair of dies. The sealed capsule was placed into a degassed graphite crucible and then placed in the impulse furnace. It was

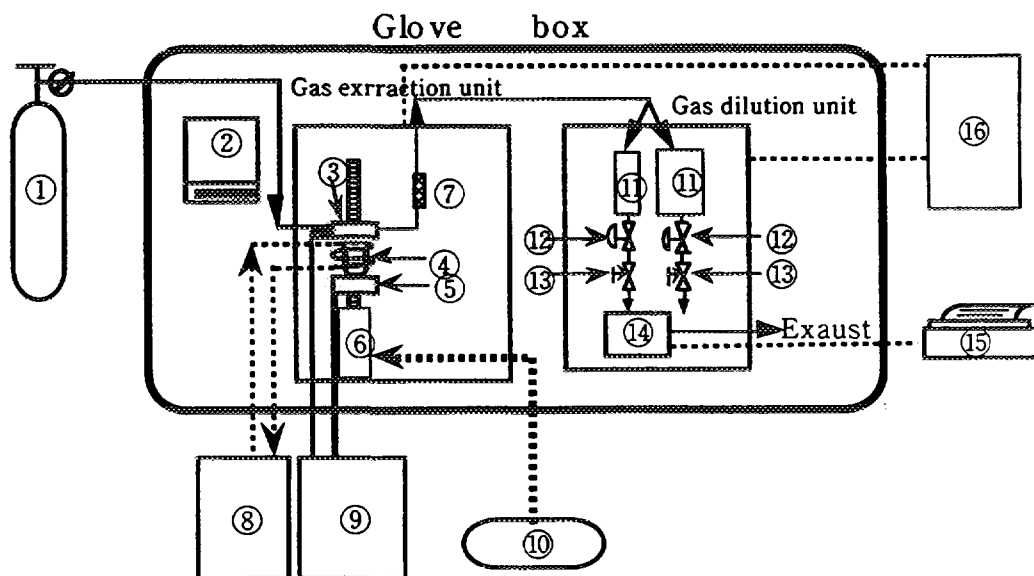


Fig. 1. Schematic diagram of O/M analysis apparatus. ① Helium bomb; ② Balance; ③ Upper electrode; ④ Graphite crucible; ⑤ Lower electrode; ⑥ Electrode driving cylinder; ⑦ Dust filter; ⑧ Refrigerator; ⑨ Power supply; ⑩ Compressor; ⑪ Gas dilution vessel; ⑫ Pressure regulator; ⑬ Needle valve; ⑭ Nondispersive infrared spectrophotometric detector; ⑮ Integrator; ⑯ Operating controller.

continually heated at about 2000°C for 30 s and 2500°C for 30 s in a current of helium gas. The O₂ in the sample was quantitatively reacted with carbon in the graphite crucible, and the CO was evolved. These gases were transferred to the buffer vessel and diluted by helium carrier gas. The CO diluted was determined using the NDIR, and the peak-area was integrated using a computerized integrator. The concentration of O₂ in the nickel capsule and the crucible was analysed beforehand and this blank value was deducted from the sample analysis value. The O/M of the sample was calculated using the following equations:

$$C_o = \frac{M_o}{M_c + M_o} \times C_{co} \dots\dots\dots (1)$$

$$C_o = \frac{M_o X}{M + M_o X} \times 100 \dots\dots\dots (2)$$

$$X = \frac{C_o \cdot M}{100 - C_o} \times 1/M_o \dots\dots\dots (3)$$

where C_o is the concentration of O₂ in the sample (wt%), C_{co} is the analysis result of CO using the present method (wt%), M_o and M_c are the atomic weights of O₂ and carbon, M is the mean atomic weight of metal in the sample, and X is the O/M ratio. Equation (3) was derived from equation (2).

2.2 RESULTS

2.2.1 Calibration curve

The calibration curve for the determination of O₂ was obtained using a O/M = 2.00 controlled MOX fuel by varying the weight over the range of 10 to 60 mg. The calibration curve obtained is shown in Fig. 2. The calibration curve gave good linearity in the range of 1.2 to 7.2 mg for the theoretical value of oxygen content.

2.2.2 Comparison with gravimetric method and precision

The O/M ratio measurement for the sintered MOX fuel pellet containing less than 10% plutonium has been determined using the oxidation weighing method [1]. On the other hand, for sintered MOX fuel containing more than 10% plutonium the O/M ratio has been determined using the oxidation-reduction method [2,3]. These methods are based on gravimetry.

In order to compare the gravimetric method and presented method, sintered MOX fuels containing about 3% plutonium was used. Moreover, accuracy of this method was measured using 25% plutonium MOX. The measurement results of the O/M ratio are shown in Table I and Table 2. The result of the present method was in good agreement with the gravimetric methods. The RSD was less than 0.20%, and the time required for one determination was about 10min for all analytical operations

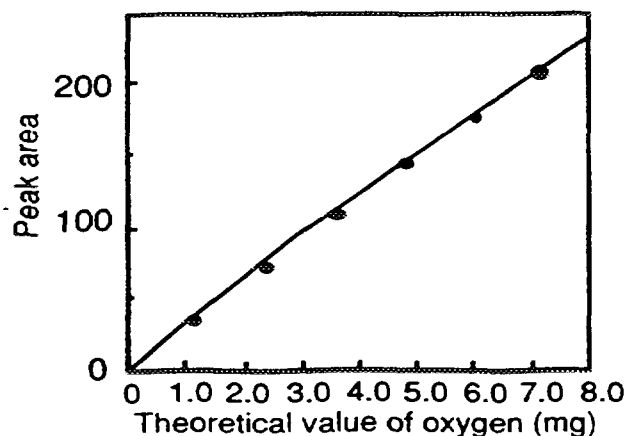


Fig. 2. Calibration curve for oxygen.

TABLE 1 Comparison of the gravimetric method and the present method for O/M analysis in 3% plutonium MOX

Method	O/M ratio ^a
Gravimetric method	2.003 ₉ ± 0.003 ₄
Present method	2.004 ₁ ± 0.003 ₇

a Mean ± standard deviation (n = 8)

TABLE 2 Determination of O/M in 25% plutonium MOX by the present method

Expt. No.	O/M ratio
1.	1.975
2.	1.985
3.	1.977
4.	1.980
5.	1.984
6.	1.978
7.	1.977
8.	1.981
Mean Value	1.979 ₆
SD	0.003 ₅
RSD (%)	0.179

SD Standard deviation

RSD Relative standard deviation

3. DETERMINATION OF OCCLUDED GAS COMPONENT ANALYSIS IN MOX USING GAS SAMPLING UNIT AND GAS CHROMATOGRAPHY

The gases extracted from the sample at vacuum condition were injected into a gas chromatograph through an originally developed gas sampling unit (GSU). The gases were simultaneously determined using the improved gas chromatograph equipped with several separation columns and a photo-ionization detector (PID). The relative standard deviations ($n=10$) were 1.0, 3.4, 0.6, 1.0, 1.4, 0.8 and 0.9% for H_2 , O_2 , N_2 , CH_4 , CO_2 , CO and C_2H_6 , respectively. The gases H_2 , O_2 , N_2 , CH_4 , CO_2 and CO from the MOX fuel pellets were simultaneously determined in this study. The results of gas analysis using this method were in agreement with that of the high temperature vacuum extraction method in the range less than $300\mu l$ of extracted gas [4].

3.1 EXPERIMENTAL

3.1.1 The gas components analysis apparatus

The gas components analysis apparatus consists of a gas extraction unit, a gas collection and a volumetric measurement unit, the GSU, the gas chromatograph and a computerized integrator. Except for the GSU and the gas chromatograph, this apparatus has been widely used for the volumetric analysis of total gas in nuclear fuel pellets by the high temperature vacuum extraction method [5]. The schematic diagram of the apparatus is shown in Fig.3. The GSU consists of special three-way and four-way valves, a buffer vessel for pressure change and a reference gas injection port, as shown in Fig. 4. Both valves were connected to glass capillary tube of i.d.2mm. The GSU could be connected with the gas collection and volumetric measurement units at vacuum condition ($10^{-2}Pa$) and the gas chromatograph at carrier gas pressure ($2 \sim 5Kg/cm^2$) without pressure change of the system and chromatogram fluctuation. The gas chromatograph (Hitachi, GC-3000, Tokyo, Japan) and a computerized integrator (Hitachi, D-2500) were used in our experiments. For gas separation, $4.0m \times 3mm$ i.d. stainless steel columns packed with Porapak Q (50 ~ 80 mesh), $2.0m \times 3mm$ i.d. stainless steel columns packed with Molecular sieve 5A(60 ~ 80 mesh) and $2.0m \times 3mm$ i.d. stainless steel columns packed with Chromosorb W(60 ~ 80 mesh) were used. In order to regulate the retention time, an empty stainless steel column of $2.0m \times 3mm$ i.d. was used.

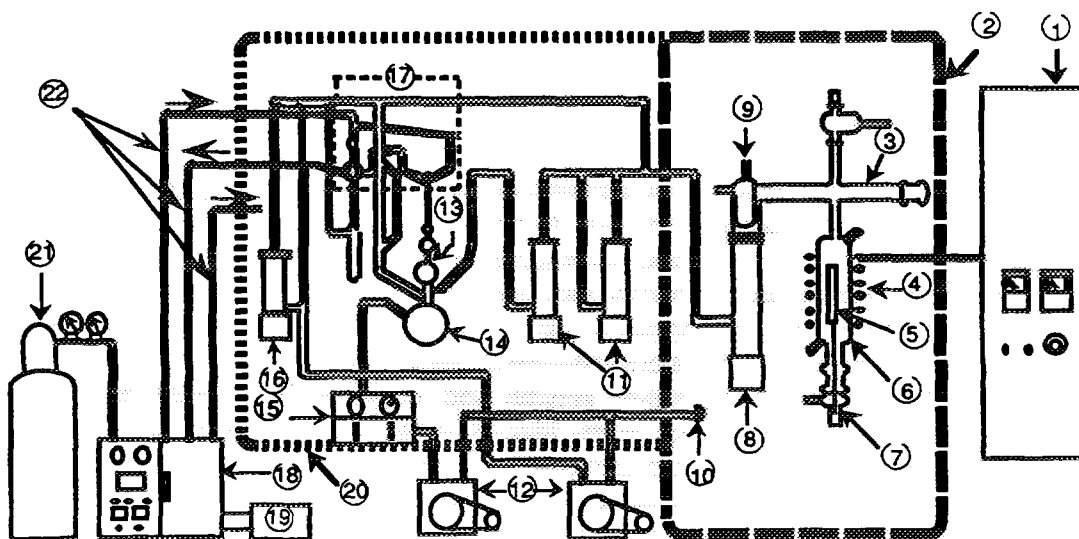


Fig.3. Schematic diagram of gas extraction and analysis apparatus.

- ①,High frequency induction equipment; ②,Glove box; ③,Pellets loading part; ④,Induction coil;
- ⑤, Molybdenum crucible; ⑥, Quartz furnace tube; ⑦, Pellets unloading part; ⑧, Mercury diffusion pump ;
- ⑨, Mercury trap; ⑩, Dust filter; ⑪, Mercury diffusion pump ; ⑫, Mechanical pump; ⑬, McLeod gauge;
- ⑭, Toepler pump; ⑮, Toepler pump controller; ⑯, Oil diffusion pump; ⑰, GSU; ⑱, Gas chromatograph;
- ⑲, Integrator; ⑳, Open port box; ㉑, Helium cylinder; ㉒, Helium carrier gas.

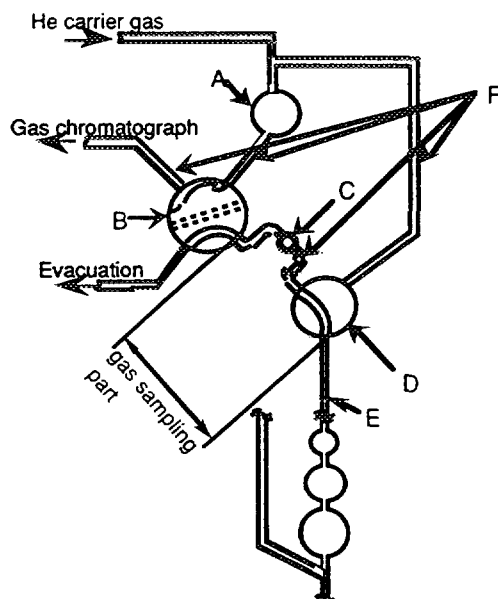


Fig.4. Gas sampling unit.

A, Spherical buffer vessel; B, Improved four-way valve; C, Reference gas injection port; D, Improved three-way valve; E, MacLeod gauge; F, Glass capillary tube of 2mm i.d.

3.1.2 Procedure of gas analysis by the gas chromatograph

The gases extracted could be simultaneously analyzed by the combination of several stainless steel columns of Porapak Q, Molecular Sieve 5A and Chromosorb W. When the objective gases were injected into the column packed with Porapak Q using the GSU, these gases were separated into two groups. The gases of both groups were injected into twin separation columns in a computer controlled flow through a changing valve. The gases of the first group (H_2 , O_2 , N_2 and CO) were separated by the column packed with Molecular Sieve 5A, and those of the other group (CH_4 , CO_2 and C_2H_6) by the column packed with Chromosorb W. Each of the separated gases was detected by the PID. A schematic diagram of the gas chromatography is shown in Fig. 5.

3.2.3 Measurement procedure

The weighed sample (about 1g) was transferred into the pellets loading part of the apparatus, which was evacuated to approximately 10^2 Pa using the mercury diffusion pump and the mechanical pump. The molybdenum crucible without the sample was outgassed beforehand until less than 10μ l at the S.T.P. condition. Then the sample was dropped into the molybdenum crucible and heated at $1700^\circ C$ for 30 min. The released gas from the sample was corrected to the McLeod gauge using the mercury diffusion pump and the toeppler pump, where the temperature and pressure were measured. The total gas volume of the sample was calculated from the temperature, pressure and volume of the collected gas at the S.T.P. condition. Volumetrically measured gas by the McLeod gauge was transferred into the GSU. The extracted gas was injected into the gas chromatograph at the same pressure as the carrier gas, and analysed by the PID. The total volume of the gas occluded per unit mass in the sample at the S.T.P. was obtained as the sum of all components of the gas analysed.

3.2 RESULTS

3.2.1 Determination of occluded gases in MOX fuel pellets

Occluded gases in the MOX fuel pellets were quantitatively and qualitatively analysed. As a results of the standard gas analysis and verification of the retention time, the peaks were qualitatively

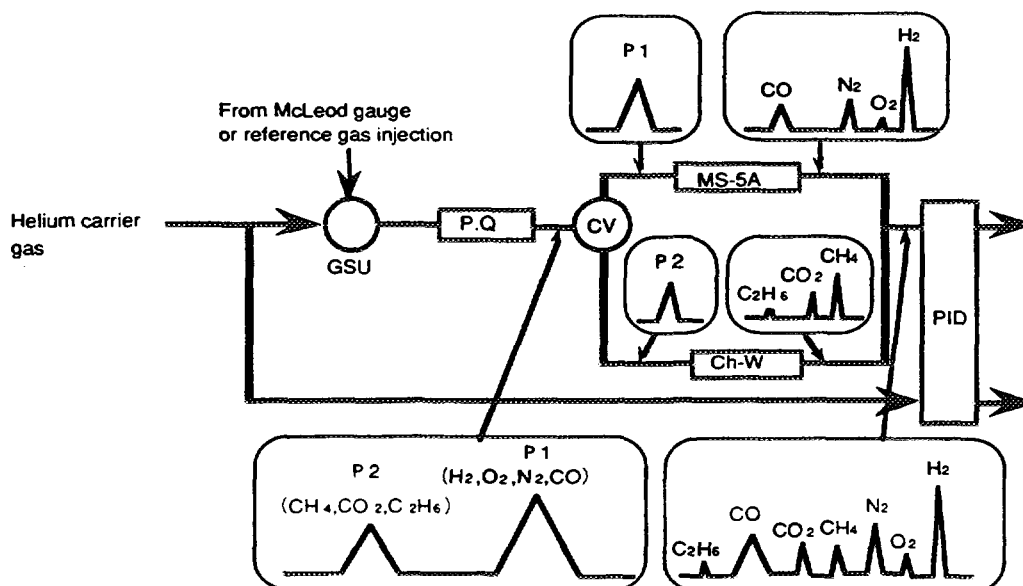


Fig.5. Principle of gas separation using gas chromatograph.

GSU, gas sampling unit; MS-5A, Separation column with Molecular Sieve 5A
 CV, Flow through changing valve; Ch-W, Separation column with Chromosorb W;
 P.Q, Separation column with Porapak Q; PID, Photoionization detector.

analysed as H_2 , O_2 , N_2 , CH_4 , CO_2 and CO . Further, concentrations of the objective gases in the MOX fuel pellets were quantitatively determined. The obtained results are shown in Table 3. From these experiments, as to the sintered pellets in hydrogen-nitrogen (5% - 95%) atmosphere, H_2 , N_2 and CO were found to be main component gases. On the other hand, for the sintered pellets in hydrogen-argon (5% - 95%) atmosphere, H_2 and CO were the main component gases. C_2H_6 was not detected. A typical gas chromatogram of occluded gases in the MOX fuel pellets is shown in Fig.6.

TABLE 3 Analytical results of occluded gases in MOX fuel pellets

Lot No.	Sintering Atmosphere	Found ^a ($\mu\text{l/g}$)						
		H_2	O_2	N_2	CH_4	CO_2	CO	C_2H_6
1.	$H_2 - N_2$ (5% - 95%)	46	-- ^b	20	-- ^b	-- ^b	9.4	ND ^c
2.	$H_2 - Ar$ (5% - 95%)	14	-- ^b	-- ^b	-- ^b	-- ^b	1.9	ND ^c
3.	$H_2 - Ar$ (5% - 95%)	14	-- ^b	-- ^b	-- ^b	-- ^b	12	ND ^c
4.	$H_2 - N_2$ (5% - 95%)	93	0.5	38	-- ^b	-- ^b	15	ND ^c
5.	$H_2 - N_2$ (5% - 95%)	21	1.3	30	-- ^b	-- ^b	11	ND ^c

- a At S.T.P. condition
- b Less than the minimum limit of determination
- c Not detected

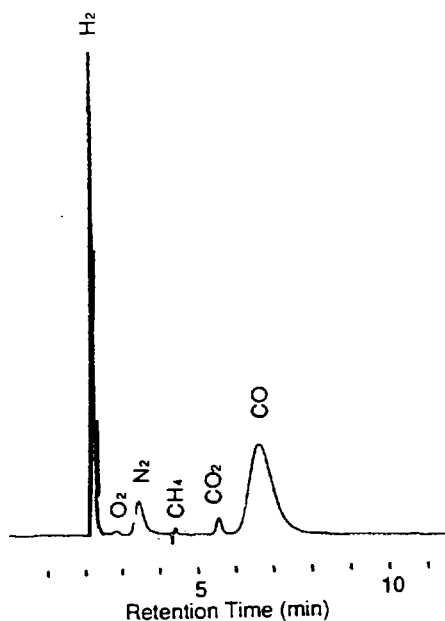


Fig.6. Typical gas chromatogram of occluded gases in MOX fuel pellets.

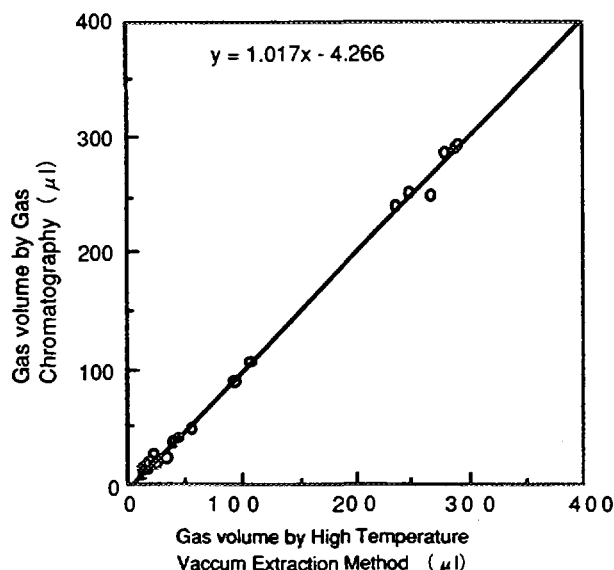


Fig.7. Correlation diagram of high temperature vacuum extraction method and extracted gas analysis by gas chromatography.

3.2.2 Comparison of the high temperature vacuum extraction method and the gas chromatography

The total volume of the occluded gases was determined for a large number of samples by the high temperature vacuum extraction method and by the present extracted gas analysis using the gas chromatography. The pellets used in this study were those fabricated for the purpose of production test of the MOX fuels. The correlation diagram of both methods is shown in Fig. 7. The correlation coefficient value was 0.998 ($n = 36$). The results of the present analysis of extracted gas using the gas chromatography were in good agreement with those of the high temperature vacuum extraction method in the range of less than $300\mu\text{l}$. Therefore, this method is applicable not only to MOX pellets but also to UO_2 pellets for the analysis of occluded gas below $300\mu\text{l}$.

4. DETERMINATION OF NITROGEN IN MOX BY GAS CHROMATOGRAPHY AFTER INERT GAS FUSION

This technique is based on chromatographic determination of nitrogen in released gases from fused sample. The sample and iron metal flux in a graphite crucible were heated to 2700°C by an impulse furnace under a helium atmosphere. From the fused sample, which was gases evolved such as H_2 , N_2 and a large amount of CO . The CO produced was interfered with the measurement of N_2 . Consequently, for N_2 separation from other gases and CO removed, a gas chromatograph equipped with a pre-cut system was originally developed. Nitrogen separated was determined using a thermal conductivity detector (TCD). The RSD was less than 5%, and the time required for one determination was about 10 min.

4.1 EXPERIMENTAL

4.1.1 Apparatus

The schematic diagram of the apparatus is shown in Fig. 8. An impulse furnace and a gas chromatograph equipped with the pre-cut system and the TCD were enclosed in the glove-box. The gas chromatograph was installed in the thermostat at 65.5°C . The pre-cut system consisted of $500\text{mm} \times 4\text{mm}$ i.d. stainless steel columns packed with Porapak N of 60 ~ 80 mesh (C-1) and $600\text{mm} \times 4\text{mm}$ i.d.

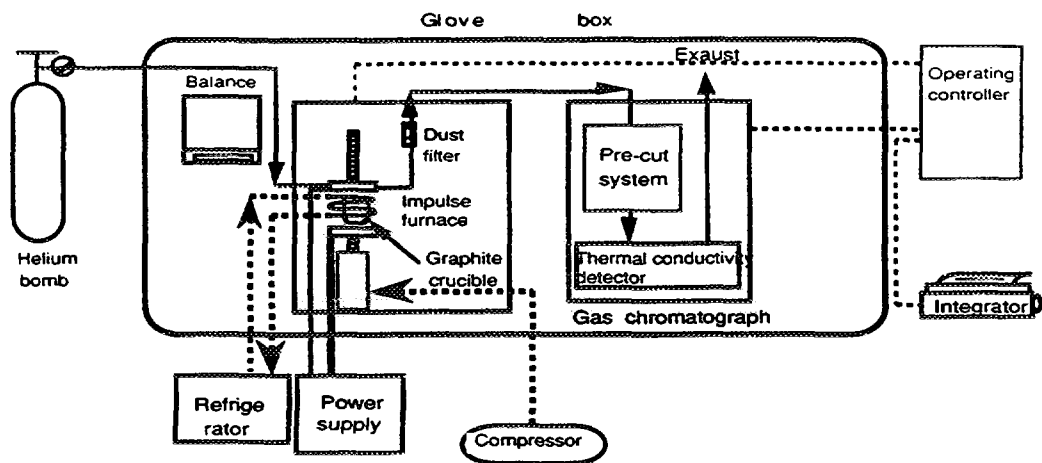


Fig.8. Schematic diagram of nitrogen analysis apparatus.

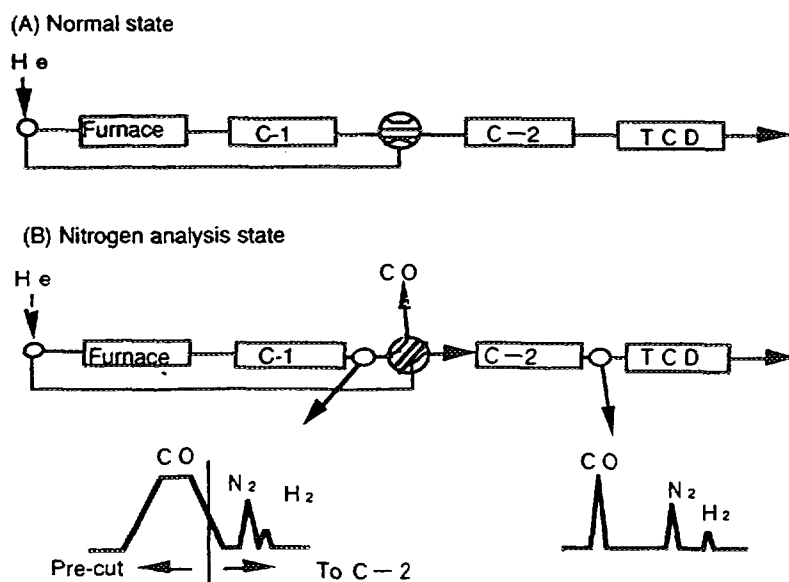


Fig.9. Schematic principle diagram of pre-cut system.
C-1, Porapak N column; C-2, Silica Gel column;
TCD, Thermal conductivity detector.

stainless steel columns packed with Silica gel of 60 ~ 80 mesh (C-2) and a carbon monoxide purge valve. The schematic diagram of the pre-cut system is shown in Fig. 9. A computerized peak-area integrator from Shimadzu Co., Ltd. CR-3A (Kyoto, Japan) was used.

4.1.2 Procedure

The sample was placed into a degassed graphite crucible, weighed to an accuracy of 0.1mg and the metal flux was added. The crucible was placed in the impulse furnace, and it was heated up to 2700°C for 30 sec under a helium atmosphere. Gases released from the sample were carried to the pre-cut system by the helium carrier gas. N₂ was determined by the TCD, and the chromatogram peak-area of N₂ was integrated by the computerized peak area integrator. The concentration of N₂ in the iron powder was analysed beforehand, and this blank value was subtracted from the sample analysis value. The calibration curve for N₂ was made using the N₂ standard gas or the standard materials.

4.2 RESULTS AND DISCUSSION

4.2.1 Calibration curve

The Japanese Standards of Iron and Steel (JSS) were used as the standard materials, which were purchased from the Iron and Steel Institute of Japan. The certified nitrogen analysis values of JSS 366-6, JSS 023-3, JSS 368-6 and JSS 153-7 were 9ppm, 39ppm, 129ppm and 165ppm, respectively.

The calibration curve for the determination of nitrogen was prepared using the standard materials. The calibration curve obtained was linear in the range of 9 to 165ppm.

4.2.2 Comparison of the Kjeldahl method with the present method

In order to compare the Kjeldahl method with the present method, the two sintered pellets used in this study were fabricated for the purpose of production testing of the MOX fuels. The N₂ contents in these pellets were adjusted to be higher than that generally used in the MOX fuels. The plutonium contents of two pellets were 2% for the sample A and 30% for the sample B. The analytical results of N₂ values for sample A and sample B are summarized in Table 4. In both methods, the mean values and the standard deviation were 65.3 ± 9.2 ppm and 77.1 ± 3.1 ppm for sample A and 152.5 ± 18.7 ppm and 156.6 ± 7.4 ppm for sample B, respectively. The results obtained by the Kjeldahl method were lower than those of this method. The RSD of this method were less than 5%.

In the Kjeldahl method, which is based on complete conversion to ammonia ions of the N₂ contained in the sample, the dissolution process for the sample is very important. For uranium metal, uranium dioxide and uranium nitrides, Lathouse et al. have shown that loss of N₂ can occur in the dissolution process for the Kjeldahl method [6]. For uranium nitride composed of the UN phase, Takahashi has shown that the results obtained by the Kjeldahl method is lower by about 5% than those obtained by the Dumas method [7]. Compared to the uranium dioxide pellets, the MOX fuel is slightly soluble in acid solutions because of the coexistence of plutonium, and loss of N₂ can occur in the dissolution process. Therefore, the analytical results of N₂ by the Kjeldahl method can show a low value compared to the present method.

TABLE 4 Comparison of the Kjeldahl method with the present method

Method	Sample No.	Nitrogen found, ppm ^a
Kjeldahl method	A	65.3 ± 9.2
	B	152.5 ± 18.7
Present method	A	77.1 ± 3.1
	B	156.6 ± 7.4

a Mean \pm standard deviation, 10 results

4. CONCLUSION

- (1) The O/M analysis method for MOX fuel was developed using nondispersive infrared spectrophotometry (NDIR) after inert gas fusion. The result of the present method was in good agreement with the gravimetric methods. The RSD was less than 0.20%. and the time required

for one determination was about 10min for all analytical operations. This method is applicable to sintered MOX fuels over a wide range of plutonium content.

- (2) The gases were simultaneously determined using an originally developed GSU, the improved gas chromatograph equipped with several separation columns and PID. The RSD were 1.0, 3.4, 0.6, 1.0, 1.4, 0.8 and 0.9% for H₂, O₂, N₂, CH₄, CO₂, CO and C₂H₆, respectively. The gases H₂, O₂, N₂, CH₄, CO₂ and CO from the MOX fuel pellets were simultaneously determined. The results of gas analysis using this method were in agreement with that of the high temperature vacuum extraction method in the range less than 300 μ l of extracted gas .
- (3) The nitrogen analysis method for MOX fuel was developed using a gas chromatograph equipped with a pre-cut system and TCD. The RSD was less than 5%, and the time required for one determination was about 10 min.

5. FUTURE PLANS

In order to put these analysis technologies for MOX to practical use, further improvements are necessary. Particularly, the developments of automatic handling system, simultaneous determination methods for impurity and more accurate methods need to be proceed.

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