



最終講義 2013.3.7(工学部一号館201講義室)



「分光の夢を追いつつ四拾年虹の七色まだ見えず」

エコトピア科学研究所エネルギー科学研究部門
応用化学分野エネルギー変換化学講座
北川邦行

- 分光分析研究時代
- <学生時代>
- ○原子分光分析法研究(主に解析)
- * 竹内次夫先生の指導の下、卒業研究において、容量結合性マイクロウェーブプラズマ発光分光分析；共存元素による干渉(おもに、アルカリ・アルカリ土類元素による増感効果)について研究した。励起温度、イオン率の測定方法を確立、後にトイレの中で思い付いた、補正のための4線法は修士研究の1つとなった。
- * 原子化器(火炎＆電気加熱)の分光解析；励起温度、原子化率の測定を発光、吸光方で行い化学干渉の基本パラメータの測定に成功した。競合者にSturgeon先生がいた。三重大学の太田先生や我妻先生らも原子吸光による励起温度の計測の研究をされた。



Analytical Chemistry

- *History & Essence* -

分析化学—歴史と真髄

Japan Society for
Analytical Chemistry → Analytical Sciences
分析化学 分析科学

应用計測化学

Solitons with chaos

Hand Analyses Gravimetric

手分析 | 重量分析
容量分析
Volumetric



図 6-3 戻過の方法



図 6-12 水化の際のる
つぼのおき方

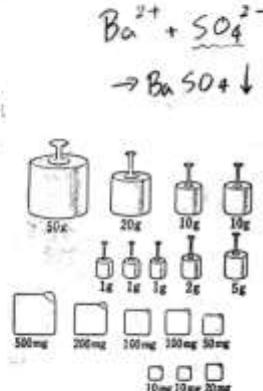


図 3-3 分 量

⇒ 構造分析

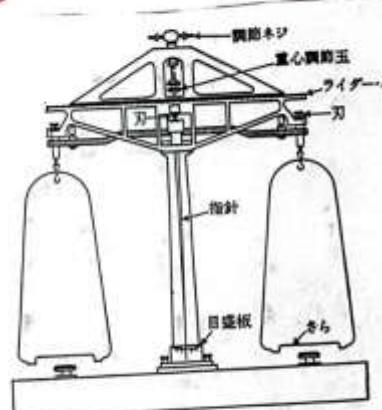
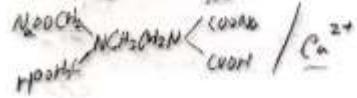
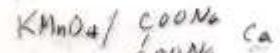
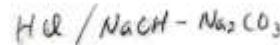
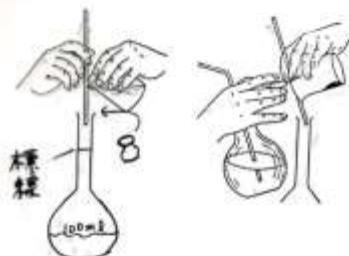


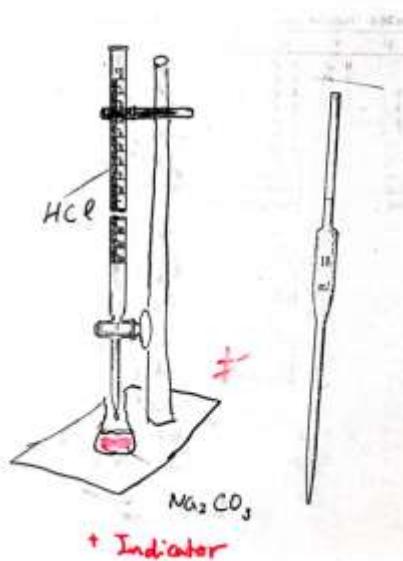
図 3-1 化学ハカリ



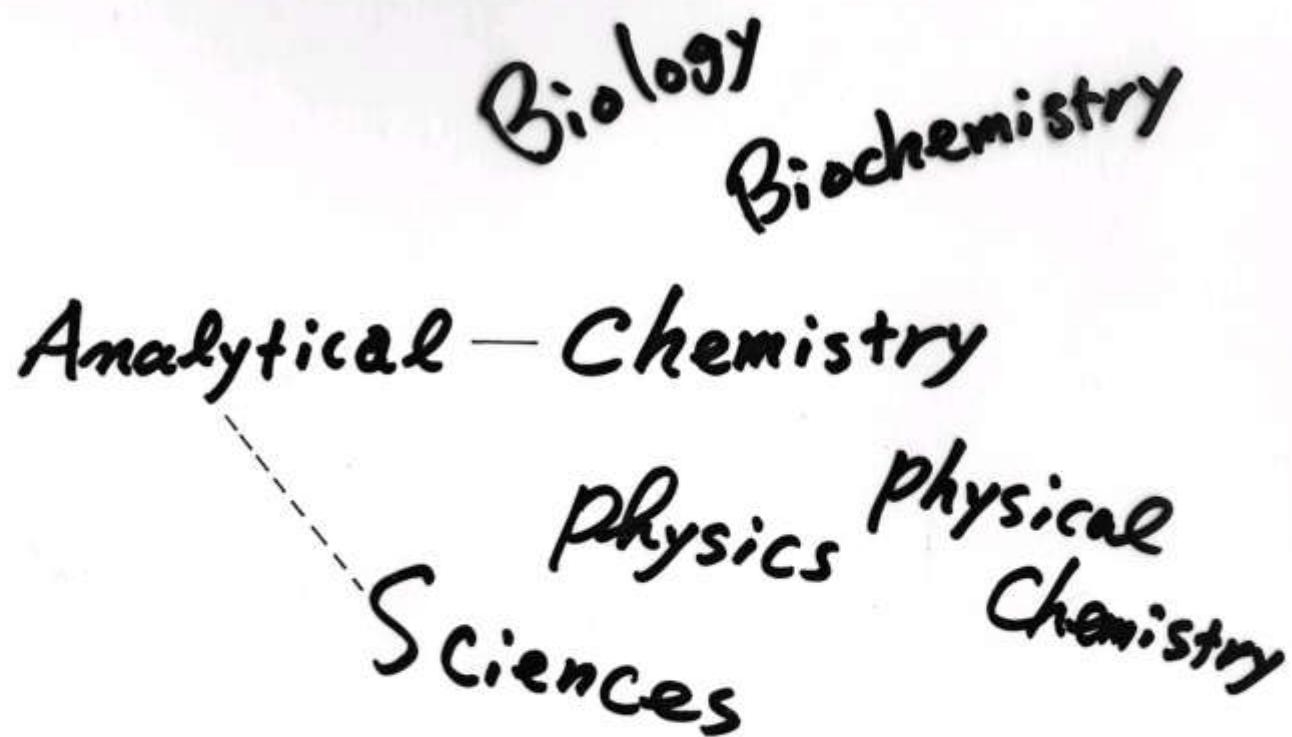
H₃O⁺

NH₃⁻

H₃O⁺



Technology



International Congress on Analytical Sciences (ICAS)

International Conference on Atomic Spectroscopy (ICAS)

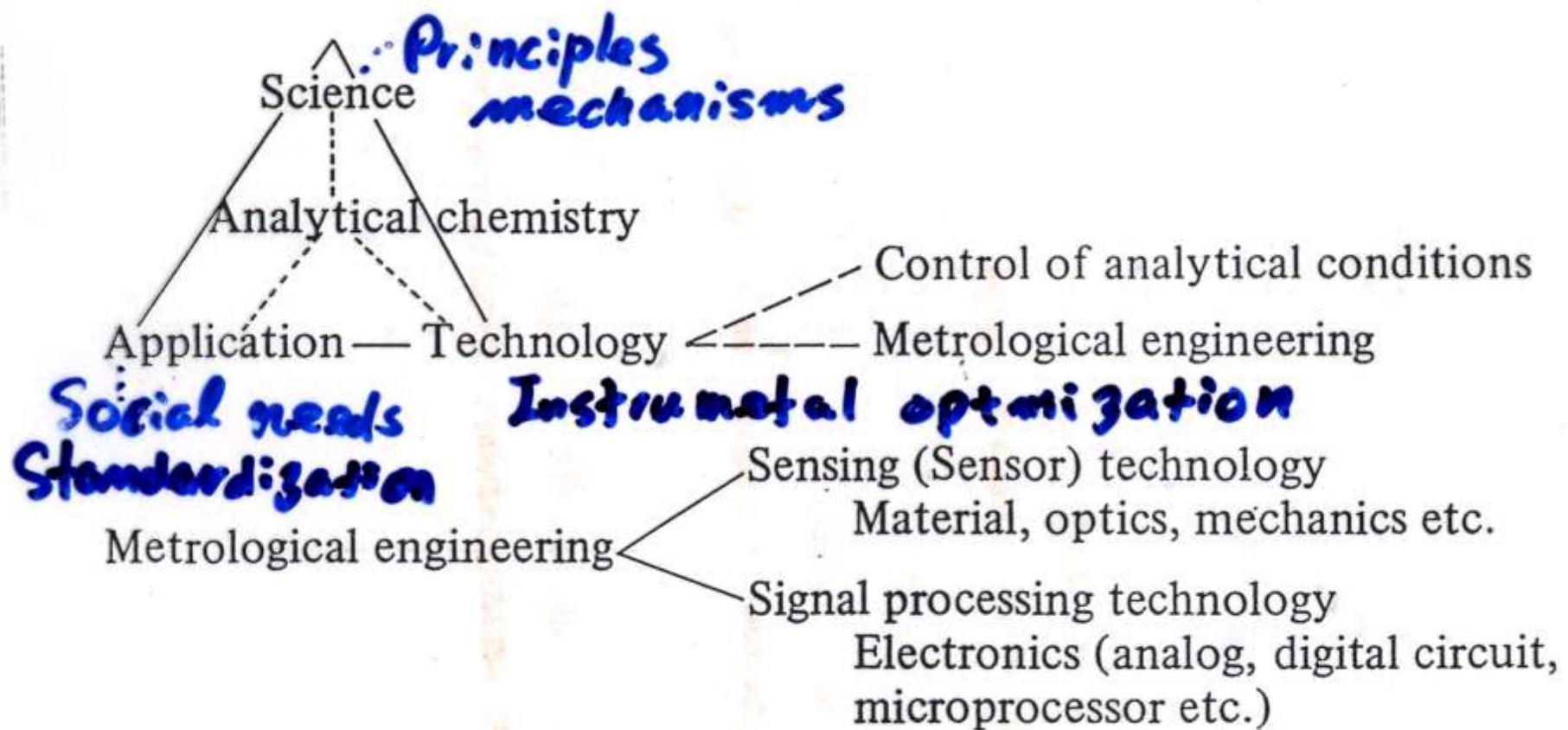
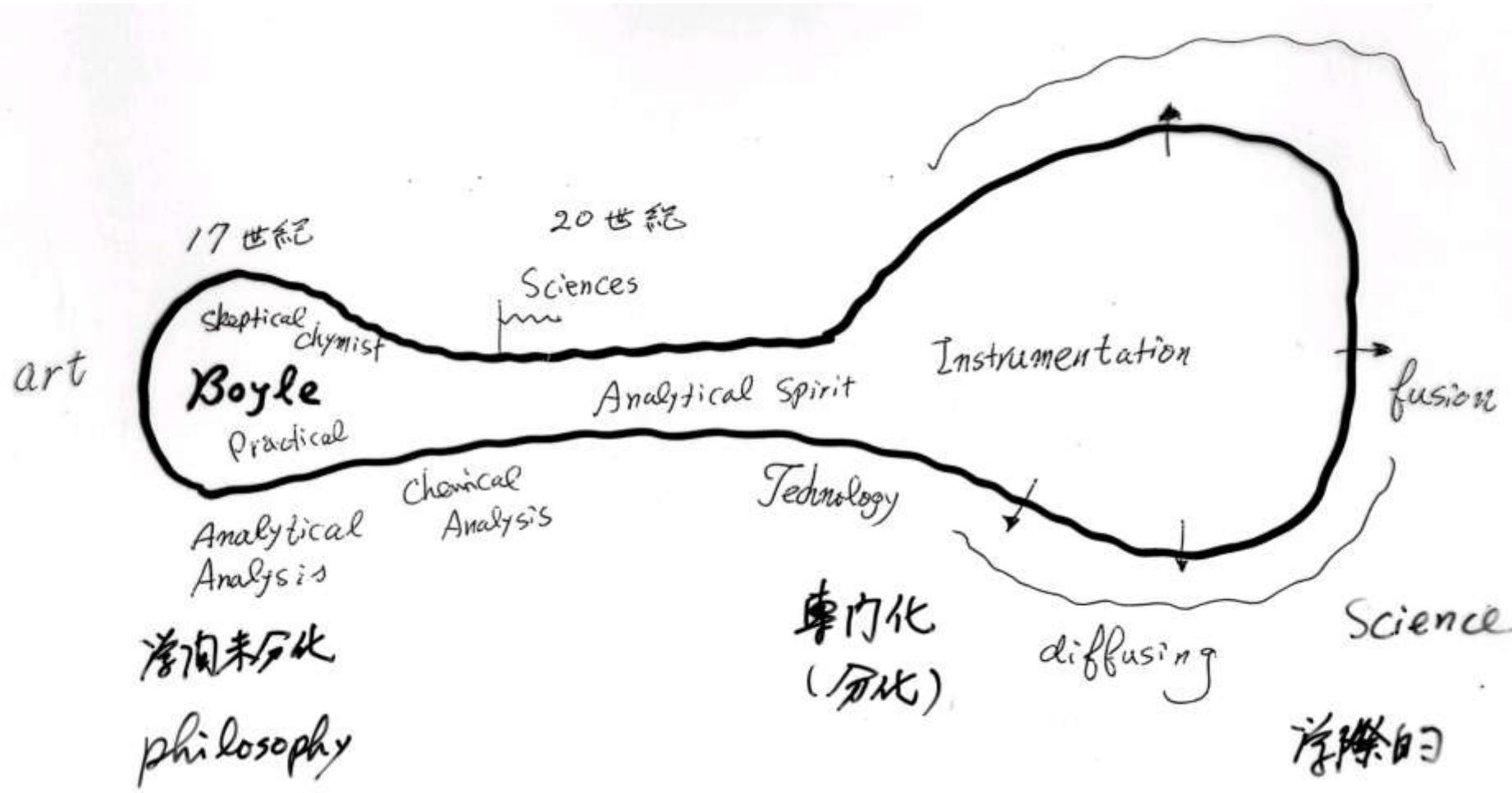


Fig. 1 Triangle of analytical chemistry



XFS

Spectroscopy

AES, AAS, AFS
AMORS, LEI, MASS...

Method-oriented

ZAAS

Optics

Excitation/Atomization Sources
Signal processing

Instrumentation

Spectrometers, Detectors
Lamps, Flames

Numerics

Archaeology

Sciences

Medical

Application

Chemical/Biological
Treatment, Engineering, Environmental

Interferences
EIE
Mechanism Study

Problem-oriented

Analytical Atomic Spectroscopy

Mechanism study
(Feedback concept)

Table 1-2 Time flow chart of the progress of an instrumental analytical method

1. Concept, theoretical basis or principle
2. Experimental verification of the concept applicability
3. Instrumental design and hardware (technological) optimization
4. Standardization and software (procedure) optimization in practical applications

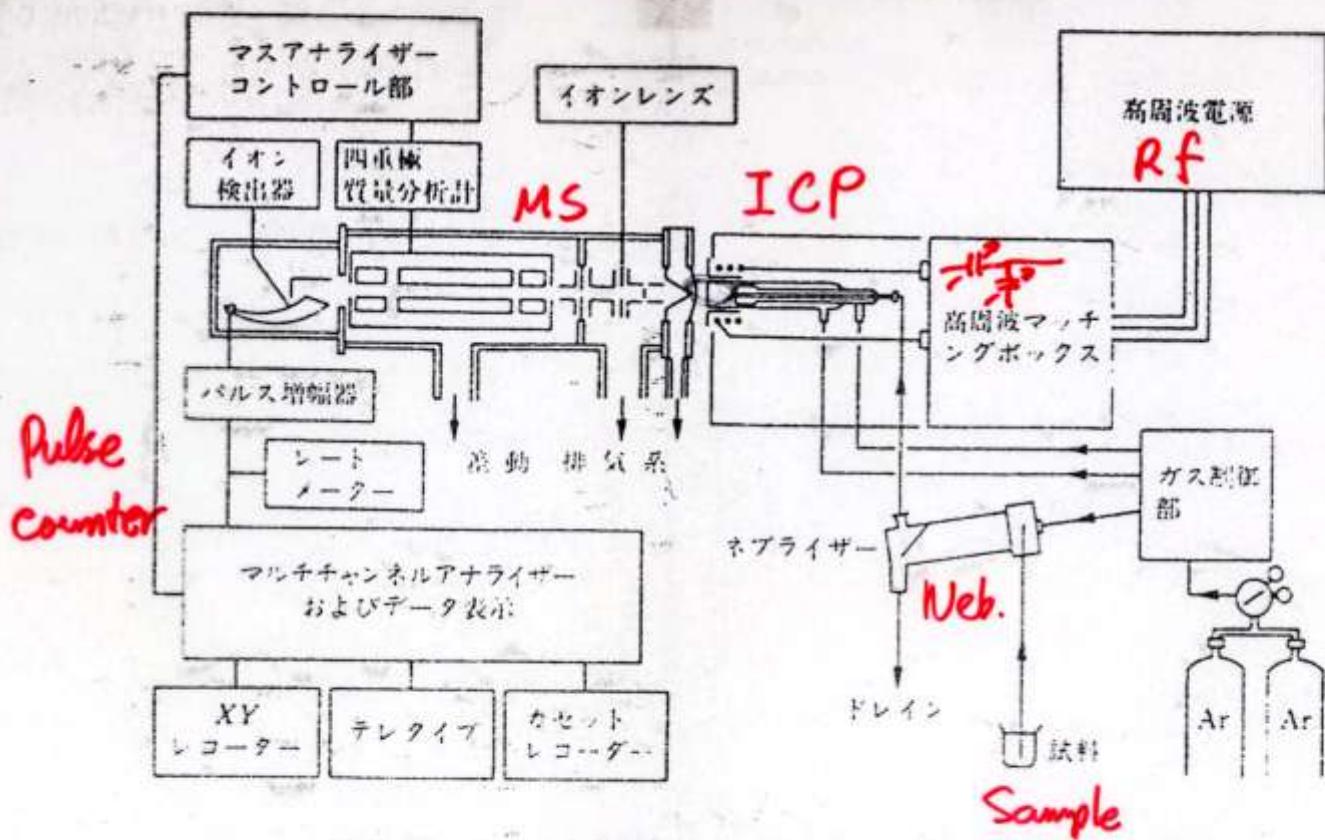
hyphenated methods

{

*Feed forward , quantum leap
non-linear*

Fig. 1.

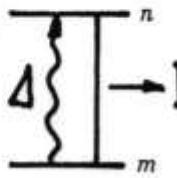
hyphenated
method



ICP-MS システムの概略図 [A. R. Date, *Trends Anal. Chem.*, 2, 225
(1983)]

Atomic emission spectroscopy

e
a



$$I = I_E + I_B$$

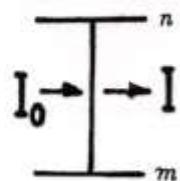
$$I_E \propto N_n \propto N_a e^{-E_n/kT}$$

Atomic absorption spectroscopy

s
c



a



$$I' = I_0 e^{-\kappa l} e^{-\beta l}$$

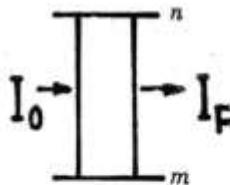
$$\int \kappa d\nu \propto N_m$$

Atomic fluorescence spectroscopy

w



a



$$I = I_F + I_B$$

$$I_F \propto I_0 N_m$$

Fig. 2 Schematic diagrams of principle for three kinds of atomic spectroscopy (as for detailed theory, refer to the main text in Chapter 2)

Table 2 Components of analytical atomic spectroscopy

Spectroscopy	Atomization/excitation source
Atomic emission spectroscopy	Chemical flames (air-C ₂ H ₂ , air-H ₂ etc.)
Flame photometry	Electric discharges
Arc/spark emission	Spark
Inductively coupled plasma	Arc DC, AC, RF, microwave Glow discharge Inductively coupled plasma Capacitively coupled plasma Microwave induced plasma etc.
Atomic absorption spectrometry	Electrothermal atomizer
Zeeman AAS	Cold vapor
Atomic fluorescence spectroscopy	Dispersion systems Detectors Electronics
Atomic magneto-optical rotation spectroscopy	Light sources (hollow cathode lamp, electrodeless discharge lamp etc.)
Multi-line method	

Table 3 Brief chronology of analytical atomic spectroscopy

	AES	AAS	AFS
1666	Light dispersion (Newton)		
1860	Flame photometry (Bunsen & Kirchhoff)	1802 Reversal line (Wollaston) 1815 Fraunhofer line (Fraunhofer)	
1890s-		1896 Zeeman effect (Zeeman)	
1930s	Spark/arc-AES, various types of monochromator		1924 Atomic fluorescence (Nicho
1961	Prototype of ICP (Reed)	1955 AAS concept (Walsh & Alkemade et al.) 1955-62 Basic development/many patents in Australia and New Zealand 1961 ETA (L'vov) 1962-69 Explosive growth, commercially available systems	
1962-69	Basic development, detection limit (Fassel et al.)		1963 Prediction of AFS (Alkemade) 1964-69 Theory and basic development (Winefordner et al.)
1965-70	Optimization for low inter-element effect	1969-76 Standardization	1970- A commercial available non-dispersive instrument, many instrumental improvements
1970-	Mechanism study	1970- Commercially available EAT's, mechanism study	1975- Dye-laser AFS
1975-80	Explosive growth, commercially available ICP's, standardization	1971 ZAAS (Prugger, Hadeishi) 1976- Commercial available ZAAS, microprocessor	
1981	ICP-AFS	1982- New types of (separative) ETA? , trace characterization?	1981 ICP-AFS
1982-	Small sample size, miniaturization, detailed mechanism study, other types of plasmas?		1982- Removal of background scattering, ZAFS? , time-resolved AFS?

PHILOSOPHICAL TRANSACTIONS.

February 19. 1671.

THE CONTENTS.

A Letter of Mr. Isaac Newton, Mathematick Professor in the University of Cambridge; containing his New Theory about Light and Colors: Where Light is declared to be not Similar or Homogeneal, but consisting of differnt rays, some of which are more refrangible than others: And Colors are affirm'd to be not Qualifications of Light, deriv'd from Refractions of natural Bodies, (as 'tis generally believed;) but Original and Connate properties, which in divers rays are divers: Where several Observations and Experiments are alledged to prove the said Theory. An Accomp't of some Books: I. A Description of the EAST-INDIAN COASTS, MALABAR, COROMANDEL, Ceylon, &c. in Dutch, by Phil. Baldeus. II. Antonii le Grand INSTITUTIO PHILOSOPHIAE, secundum principia Renati Des-Cartes; nova methodo adornata & explicata. III. An Essay to the Advancement of MUSICK; by Thomas Salmon M.A. Advertisement about Thacon Smyrnaeus. An Index for the Translations of the Year 1671.

A Letter of Mr. Isaac Newton, Professor of the Mathematicks in the University of Cambridge; containing his New Theory about Light and Colors: sent by the Author to the Publisher from Cambridge, Febr. 6. 1671; in order to be communicated to the R. Society.

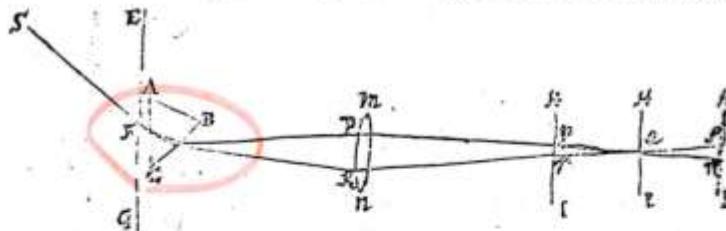
SIR,
To perform my late promise to you, I shall without further ceremony acquaint you, that in the beginning of the Year 1666 (at which time I applied myself to the grinding of Optick glasses of other figures than Spherical,) I procured me a Triangular glass-Prisme, to try therewith the celebrated Phænomena of

G 3 3 3

Colours.

about three foot radius (suppose a broad Object-glass of a three foot Telescope,) at the distance of about four or five foot from thence, through which all those colours may at once be transmitted, and made by its Refraction to converge at a further distance of about ten or twelve feet. If at that distance you intercept this light with a sheet of white paper, you will see the colours converted into whiteness again by being mingled. But it is requisite, that the Prism and Lens be placed steady, and that the paper, on which the colours are cast, be moved to and fro: for, by such motion, you will not only find, at what distance the whiteness is most perfect, but also see, how the colours gradually converge, and vanish into whiteness, and afterwards having crossed one another in that place where they compound Whiteness, are again dissipated, and severed, and in an inverted order retain the same colours, which they had before they entered the composition. You may also see, that, if any of the Colours at the Lens be intercepted, the Whiteness will be changed into the other colours. And therefore, that the composition of whiteness be perfect, care must be taken, that none of the colours fall besides the Lens.

In the annexed design of this Experiment, A B C expresseth the Prism set endwise to sight, close by the hole F of the window



E G. Its vertical Angle A C B may conveniently be about 60 degrees: M N designeth the Lens. Its breadth $\frac{1}{2}$ or 3 inches. S F one of the straight lines, in which differnt Rays may be conceived to flow successively from the Sun. F P, and F R two of those Rays unequally refracted, which the Lens makes to converge towards Q, and after decollation to diverge again. And H I the paper, at divers distances, of which the colours are projected: which in Q constitute Whiteness, but are Red and Yellow in R, r, and P, and Blue and Purple in P, p, and N.

If

Phil. Trans. R. S., 92, 365 (1802)

101

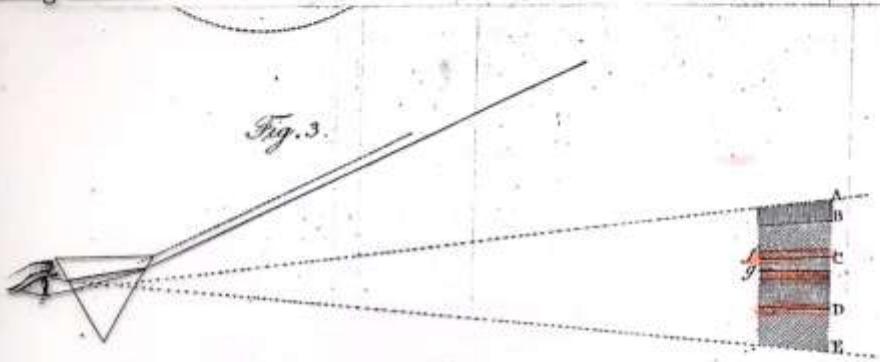
XII. *A Method of examining refractive and dispersive Powers, by prismatic Reflection.* By William Hyde Wollaston, M.D.
F.R.S.

Read June 24, 1802.

In examining the power with which various substances refract and disperse light, I have for some time past employed a method unnoticed by writers on optical subjects; and, as it is not only convenient in common cases of refraction, but also capable of affording results not attainable by other means, I have been induced to draw up a short account of the method itself, and of the most remarkable instances of its application.

This method was suggested by a consideration of Sir ISAAC NEWTON's prismatic eye-glass, the principle of which depends on the reflection of light at the inner surface of a dense refracting medium.

Fig. 3.



Ann. phys. chem., 109, 143 (1860)

Bayer.

XIV. *Ueber die Fraunhofer'schen Linien;*
von G. Kirchhoff.

(Aus d. Monatssbericht d. Berl. Acad. October 1859.)

Fraunhofer
Kirchhoff

I. *Chemische Analyse durch Spectralbeobachtungen;*
von G. Kirzhoff und R. Bunsen.

Es ist bekannt, dass manche Substanzen die Eigenschaft haben, wenn sie in eine Flamme gebracht werden, in dem Spectrum derselben gewisse helle Linien hervortreten zu lassen. Man kann auf diese Linien eine Methode der qualitativen Analyse gründen, welche das Gebiet der chemischen Reaktionen erheblich erweitert und zur Lösung bisher unzugänglicher Probleme führt. Wir beschränken uns hier zunächst nur darauf, diese Methode für die Metalle der Alkalien und alkalischen Erden zu entwickeln und ihren Werth an einer Reihe von Beispielen zu erläutern.

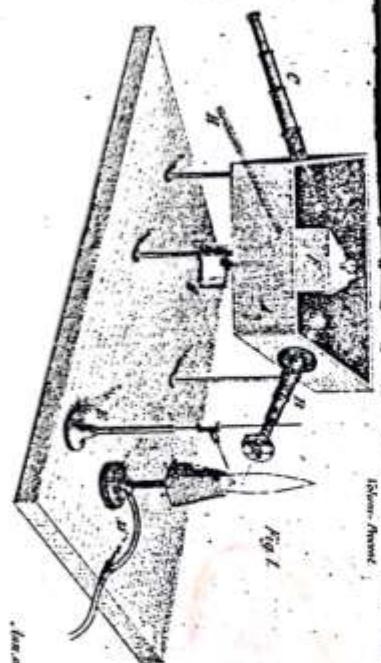
Die erwähnten Linien zeigen sich um so deutlicher, je höher die Temperatur und je geringer die eigene Leuchtkraft der Flamme ist. Die von Einem von uns angegebene Gaslampe¹⁾ liefert eine Flamme von sehr hoher Temperatur und sehr kleiner Leuchtkraft, dieselbe ist daher vorzugsweise geeignet zu Versuchen über die jenen Substanzen eigentümlichen scharfen Linien.

Auf Taf. V sind die Spectren dargestellt, welche die genannte Flamme giebt, wenn die so rein als möglich dargestellten Chlorverbindungen von Kalium, Natrium, Lithium, Strontium, Calcium, Baryum in ihr verflüchtigt werden. Das Sonnenspectrum ist, um die Orientirung zu erleichtern, beigegeben.

Die zu den Versuchen benutzte Kaliumverbindung wurde durch Glühen von chlorsaurem Kali, welches zuvor sechs bis achtmal umkristallisiert war, dargestellt.

1) Diese Annal. Bd. 100, S. 85.

Poggendorff's Annal. Bd. CX.



Ann. Phys. u. Chem. Bd. 100, S. 2

Die Spectren der Alkalien und alkalischen Erden.

Von

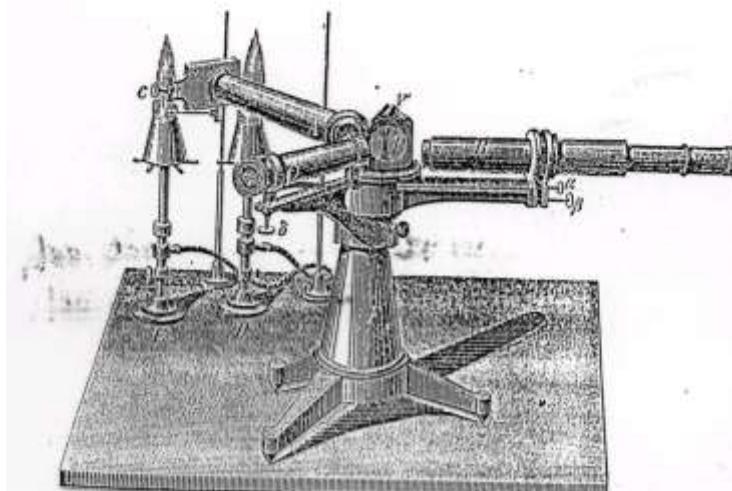
G. Kirchhoff und R. Bunsen.

In Taf. I. Fig. 1. haben wir die Metallspectren, welche von uns in zwei Abhandlungen (Pogg. Ann. Bd. 110 und Bd. 113) veröffentlicht sind, in der Ordnung zusammengestellt, welche nach dem chemischen Verhalten der Metalle die angemessene zu sein scheint. Die Zeichnungen sind unverändert geblieben bis auf eine blaue Linie im Calcium-spectrum, die wir früher nicht aufgenommen haben, da sie, den vorzugsweise characteristicischen Linien dieses Spectrums an Lichtstärke weit nachstehend, bei unvollkommeneren Apparaten schwer sichtbar ist. Bei der Vollkommenheit des in unserer letzten Abhandlung von uns angegebenen, bereits vielfach verbreiteten, Spectral-Apparates schien es uns indessen geboten, sie nicht zu übergehen, um so mehr, als man sich wiederholt versucht gefühlt hat, dieselbe einem neuen Elemente zuzuschreiben. Andere, schwächere, Linien, welche der neue Apparat in den in Rede stehenden Spectren ausser den dargestellten zeigt, haben wir nachzutragen unterlassen, weil sie bei dem practischen Gebrauch, zu dem die Tafel bestimmt ist, nur wenig Nutzen gewähren, die Auffassung des Eigenthümlichen der einzelnen Spectren aber erschweren würde.

Wir erwähnen bei dieser Gelegenheit ein Verfahren, welches bei spectral-analytischen Untersuchungen wesentlich fördernd ist. Bei dem, in Pogg. Ann. Bd. 113 von uns beschriebenen, Spectralapparate zeigt sich im Gesichtsfelde des Beobachtungsfernrohrs zugleich mit dem zu betrachtenden Spectrum eine Skale. Die einer gewissen hellen Linie entsprechende Skalenablesung ist bei denselben Apparate immer dieselbe, vorausgesetzt, dass an der Stellung der Skale und des Prismas nichts geändert wird, und abgesehen von den nur sehr kleinen Aenderungen, die durch Änderungen der Temperatur des Prismas hervorgerufen werden. Bei verschiedenen Apparaten ist aber eine Ueberein-

Fresenius, Zeitschrift. 1. Jahrgang.

I



Fresenius' Z. Anal.
Chem. I, 1 (1862).

Die Spectren der Alkalien und alkalischen Erden.

Von

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本の線からなることがわかる。

波長の長い方をD₁線、短かい
方をD₂線と呼ぶ。

3. 装置

炎光光度分析と原子吸光分
析が行える簡単な組み立て装
置が図4に示されている。

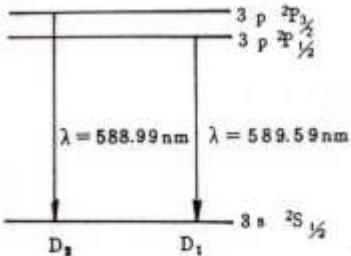


図 3

光源用電源（実験A3の原子吸光分光計のサイドパネルの）
スイッチNo.2をHVにする。

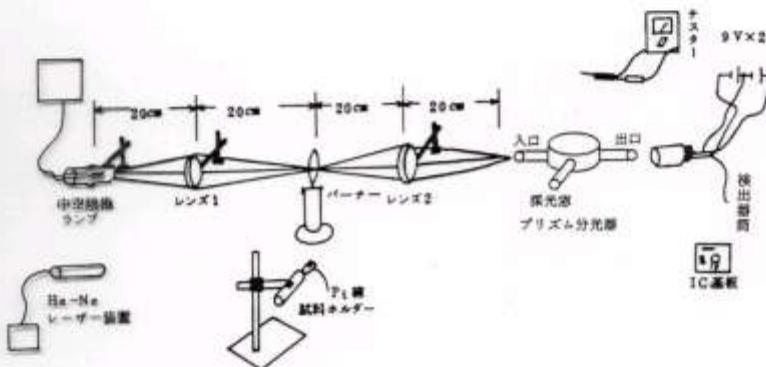


図 4

4. 実験

4-1 試薬の調製……Na₂CO₃、Li₂CO₃を正確にはかりビーカーで希塩酸に溶解し、100mL
メスフラスコに移し標準溶液 5%Na、5%Liを調製する。

$$(Na = 22.99, Li = 6.941, Cl = 35.45)$$

5%Na 標準溶液を希釈し50mL メスフラスコで1.25%Na の標準溶液を調製する。

自分の尿、唾液をビーカーに採取する。

4-2 光学調整……図4のように各光学素子を配置する際、光軸が合っていないと光が観測
されない。まず中空陰極ランプの位置にクランプでレーザー管を取り付け（中空陰極ランプ、レー
ザーパン共に振動に弱いので絶対落としてはいけない。）電源を入れレーザービームが水平に
なっているかを、ものさしで調べる（レーザー光は直接見ると目に悪影響を与えるので絶対

g resolving powers up to 15 lines per mm were made.

The spot diagrams were computed from some results² of interferometer and photographic resolving power tests obtained for a 5-inch focal length $f/5.5$ Celer type lens, the interferograms used being for off-axis positions from 8° to 16° . It was decided that sufficient rays (about 750) would be given by a square array of spacing 0.5 mm on the original interferogram of 10 mm diameter. For convenience, the original interferograms were enlarged 4 times and printed through a graticule of spacing 2 mm.

For a wave front aberration W , the transverse ray aberration given by $\partial W / \partial (\text{N.A.})$, where N.A. is the numerical aperture. The wave fronts were measured in the sagittal and tangential directions every 2 mm across the enlargement and plotted against numerical aperture. The transverse ray aberrations for each plot of the wave front were then obtained by graphical differentiation and plotted against numerical aperture. The spot diagrams were plotted from this latter set of graphs.

The photographic plates used at D were prefogged to give a density of 1.0 and the exposure time adjusted until the contrast between a resolved synthesised unit and the background was the same as the average contrast given for an easily resolved unit on a resolving power test film obtained for the lens. The emulsion of plates used was very nearly the same as the aerial film used for resolving power tests. The exposure time had to be redetermined for each spot diagram since vignetting caused the number of spots to decrease as the off-axis angle increased.

Then the normal photographic resolving power test may be simulated by printing the spot diagram through each of the test-unit masks in turn onto a separate prefogged plate.

From the results it is hoped to gain some knowledge of the influence of the emulsion upon photographic resolving power. It will also be possible to determine whether diffraction can be ignored for the large aberrations shown by this type of lens.

Double-Beam Method of Spectral Selection with Flames

C. T. J. ALKENADE AND J. M. W. MILATE

Physisch Laboratorium der Rijksuniversiteit te Utrecht, Utrecht, Holland

(Received December 27, 1954)

A NONDISPERSIVE, optic-electrical filter instrument has been developed that combines good luminosity with high spectral resolving power ($\sim 0.1 \text{ \AA}$), at wavelengths which are of practical interest in spectrochemistry. Use was made of the double-beam method, which is well known in i.r. spectroscopy. In our instrument this method was applied with a flame containing vapor of some element as a specific absorber. This flame (A in Fig. 1) was placed in one of the two light beams (I and II) which

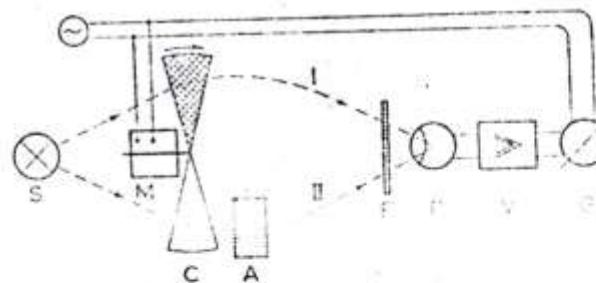


FIG. 1. S = light source to be analyzed; C = rotating disk chopping light-beams I and II in opposite phase; A = specific absorbing medium; F = auxiliary color filter; P = photomultiplier tube; G = synchronous ac measuring device.

are periodically chopped in opposite phase by chopper C . The balance of the double beam, which is detected by a photomultiplier (P) connected to a synchronous measuring device (G) is disturbed for wavelengths that are specifically absorbed by the vapor in the

The application of atomic absorption spectra to chemical analysis

A. WALSH

Chemical Physics Section, Division of Industrial Chemistry,
Commonwealth Scientific and Industrial Research Organization, Melbourne, Australia

(Received 18 January 1955)

Summary—The theoretical factors governing the relationship between atomic absorption and atomic concentration are examined and the experimental problems involved in recording atomic absorption spectra are discussed. On the basis of the discussions, it is shown that such spectra provide a promising method of chemical analysis with vital advantages over emission methods, particularly from the viewpoint of absolute analysis. It is also suggested that the absorption method offers the possibility of providing a simple means of isotopic analysis.

1. Introduction

The application of atomic spectra to chemical analysis has proved so successful over such a wide field that there is a tendency to overlook some of the basic limitations of existing methods. In spite of the remarkable advances in technique which have resulted in press-button analyses of high precision at fantastic speeds, there has been practically no progress whatsoever in solving the fundamental problem of devising an absolute method, i.e., a method which will provide an analysis without comparison with chemically analyzed standards or synthetic samples of known composition. In routine analysis for production control this problem is of little consequence, since it is only necessary to have a limited number of standards, and in such work modern direct-reading methods leave little to be desired, except on the score of complexity of equipment and associated expense. When analyses of miscellaneous materials are required, the task of providing the required range of standards becomes insurmountable and the spectrochemical method then loses its accuracy, since accurate analyses generally necessitate the use of standards which are closely similar in composition to the sample for analysis. In some analyses it is also essential that the sample and standards be similar as regards physical condition. For example, the intensity of the spectrum of a metal or alloy may vary with the metallurgical history of the sample. This difficulty may be overcome by taking the sample into solution, but accurate and sensitive methods of analyzing solutions are only available for the limited range of elements having a low excitation potential, which can be estimated by flame photometry. In this method, also, it is necessary to use standard solutions having compositions closely similar to that of the test solution.

The possibility of adapting any of the existing methods to absolute analysis does not appear to be promising. In the first place, there seems to be little prospect of developing a light source which is such that the emission spectrum of a given element is not affected by the presence in the atomic vapour of atoms of other elements. Secondly, even if these interelement effects were eliminated, there remains the problem of absolute intensity measurement and the associated problem

Atomic Magneto-optical Rotation (AMOR)

OPTIQUE. — *Sur une nouvelle action subie par la lumière traversant certaines vapeurs métalliques dans un champ magnétique.* Note de MM. D. MACALUSO et O.-M. CORBINO, présentée par M. Lippmann.

- 1. Un faisceau de lumière solaire polarisée par un premier nicol traverse le champ magnétique fourni par un électro-aimant Ruhmkorff, puis un second nicol, une lentille cylindrique, et est reçu sur un réseau concave de Rowland. Avec un oculaire muni d'un micromètre, on observe le second

Compt. Rend. Séance, 127, 548 (1898).

meter and height 15 mm). Along the central axis, a cavity in a circular truncated cone (the upper aperture 2.5 mm diameter, the lower aperture 10 mm diameter and height 15 mm) is bored to conduct the radiation from the light source to the monochromator via the atoms evolving on the glassy carbon strip atomizer. The directions of the magnetic field and the radiation are made to coincide with the Faraday configuration. The magnetic field strength can be altered by changing the distance between the pole pieces. A maximum magnetic field strength of ca. 3 kG was attainable with a gap of 5 mm between the pole pieces.



Fig. 3. The first and second authors holding the cylinder and the constructed AMORS, respectively, the two car batteries and a second author's motor car (Mitsubishi Lancer) to carry them

the intervals between measurements by switch solenoid valve (Chukyo Denki). A small cylinder 0°C and 1 atm was used to carry the whole in the car. The contents in such a small cylinder were ca. 1,000 measurements.

The overall size of the constructed $60 \times 30 \times 17$ cm and its weight is 15 kg. Figure first and second author holding the cylinder constructed AMORS, the car batteries and a second motor car (Mitsubishi Lancer) to carry them, building of our Department. Figure 4 shows the car batteries and the cylinder accommodate of the motor car. Wires connecting the batteries AMORS are to be seen. When used, the connected in series to generate 24 V. Two fuses connected in parallel are mounted in the car the motor car and charged during car running pairs of the car batteries are alternately charged car and discharged by the AMORS.

2.2 Electronic System

Figures 5 and 6 show the block diagram of system constructed and the relevant time sequences produced by timing circuits, resp. photocurrents from the photomultiplier tube (1/2 inch compact type) are amplified and converted corresponding voltages by the preamplifier amplifier IC Intersil LF356) and sent to the logic circuits.

During a short period when a hole on the cylinder intersecting the optical axis, a blank voltage corresponding to the photocurrents induced by the

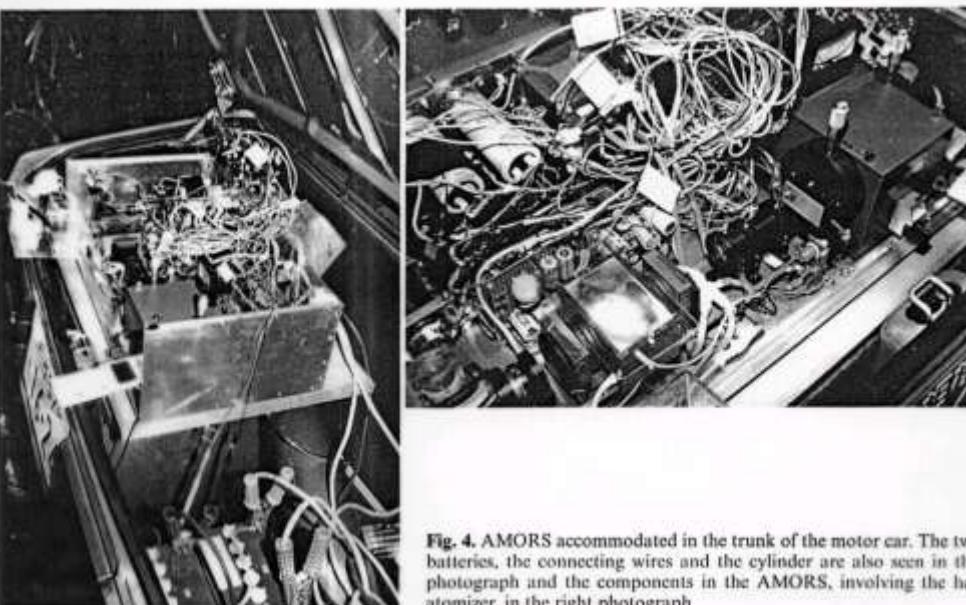
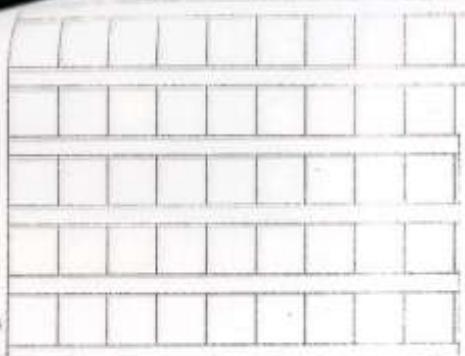


Fig. 4. AMORS accommodated in the trunk of the motor car. The two batteries, the connecting wires and the cylinder are also seen in the photograph and the components in the AMORS, involving the heated atomizer, in the right photograph



13

図 5-11 車載用小型原子磁
気旋光計 (フラグ一配置)¹¹⁾

In situ analysis

Table 3 Brief chronology of analytical atomic spectroscopy

	AES	AAS	AFS
1666	Light dispersion (Newton)		
1860	Flame photometry (Bunsen & Kirchhoff)	1802 Reversal line (Wollaston) 1815 Fraunhofer line (Fraunhofer)	
1890s- 1930s	Spark/arc-AES, various types of monochromator	1896 Zeeman effect (Zeeman)	1924 Atomic fluorescence (Nichols)
1961	Prototype of ICP (Reed)	1955 AAS concept (Walsh & Alkemade et al.) 1955-62 Basic development/many patents in Australia and New Zealand	
1962-69	Basic development, detection limit (Fassel et al.)	1961 ETA (L'vov) 1962-69 Explosive growth, commercially available systems	1963 Prediction of AFS (Alkemade) 1964-69 Theory and basic development (Winefordner et al.)
1965-70	Optimization for low inter-element effect	1969-76 Standardization	1970- A commercial available non-dispersive instrument, many instrumental improvements
1970-	Mechanism study	1970- Commercially available EAT's, mechanism study	1975- Dye-laser AFS
1975-80	Explosive growth, commercially available ICP's, standardization	1971 ZAAS (Prugger, Hadeishi) 1976- Commercial available ZAAS, microprocessor	1981 ICP-AFS
1981	ICP-AFS	1982- New types of (separative) ETA , trace characterization.	1982- Removal of background scattering, ZAFS , time-resolved AFS
1982-	Small sample size, miniaturization, detailed mechanism study, other types of plasmas		

ICP-MS, LEI, AMOR
(CFSS) PAS

ADR

原子吸光分光法の登場 (Appearance of AAS)

1955年, Walsh^[10]と Alkemade^[118]らは別々に、原子蒸気を通過するとき共鳴光が吸収され

Oh, **discharge**
plasma

something composed mainly
of blood plasma (血漿) is **plasma** (原形質)

glances
Why are you **plasma**?
(πλασμα)

Masaki

Subtle
thing
but charms
me!



Flame

Plasma--subtle thing like [?]!

cf. a Japanese traditional saying

"Woman's mind & autumn sky"

Therefore, she charms me.

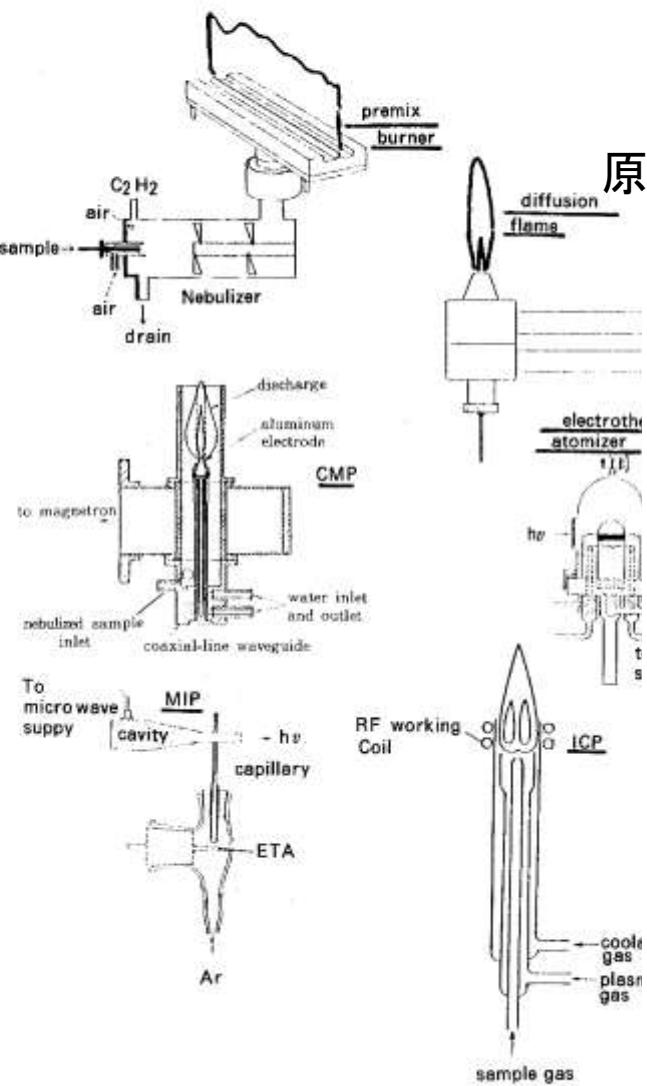


Fig. 1. Various types of atomizers and excitation sources

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原子分光分析のための原子化器・励起源

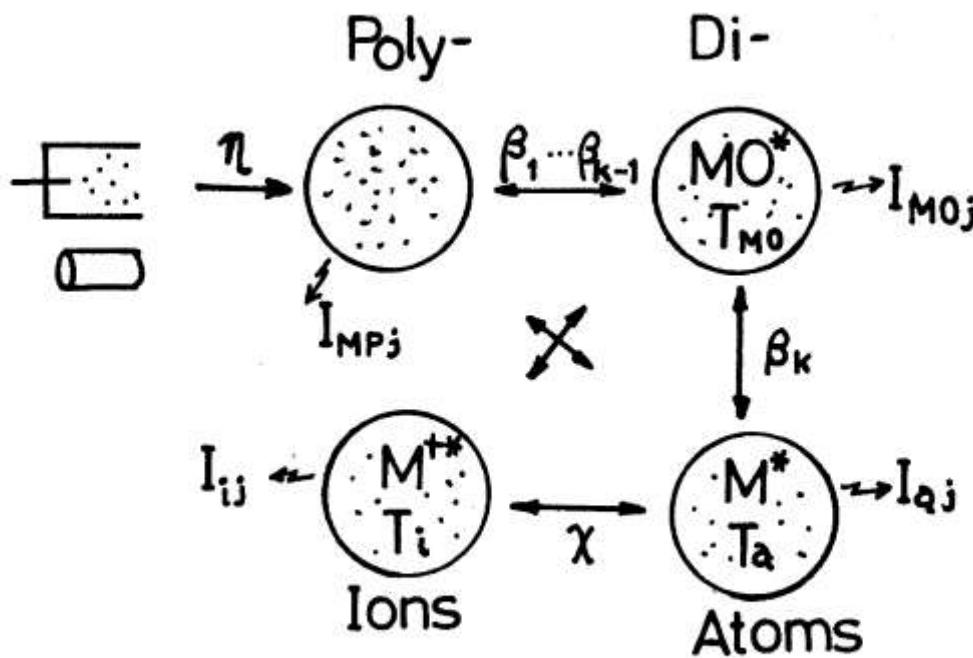


Fig. 2. Model system of atomizers and excitation sources

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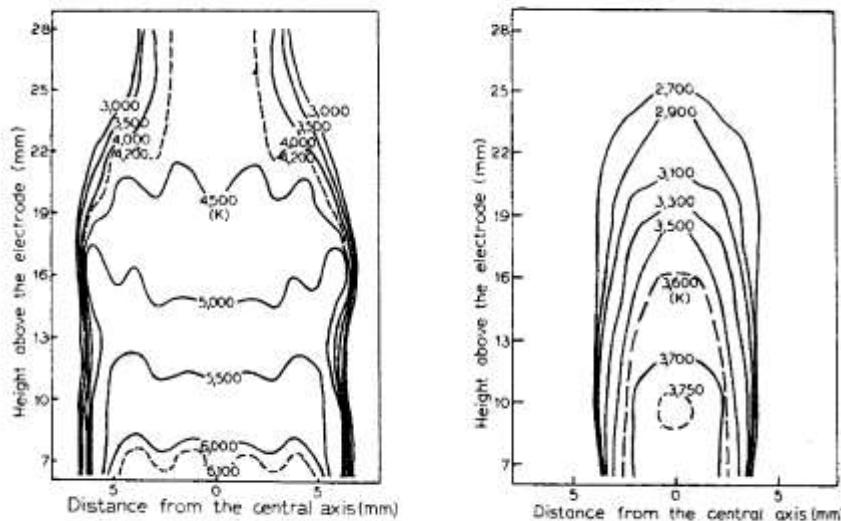


Fig. 5. Profile of excitation temperature of manganese atoms in argon plasma torch.

Fig. 6. Profile of excitation temperature of manganese atoms in nitrogen plasma torch.

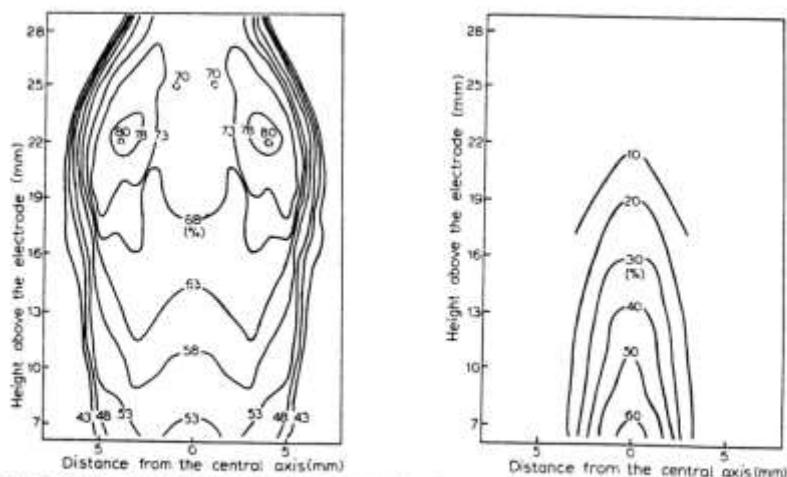


Fig. 7. Profile of degree of ionization of manganese atoms in argon plasma.

Fig. 8. Profile of degree of ionization of manganese atoms in nitrogen plasma.

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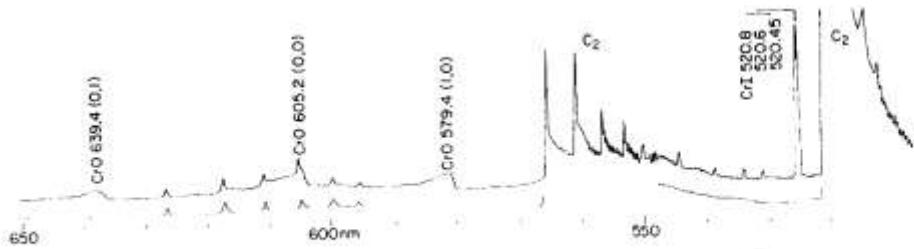


Fig. 4. Typical emission spectrum of CrO displayed on the oscillosgraph.

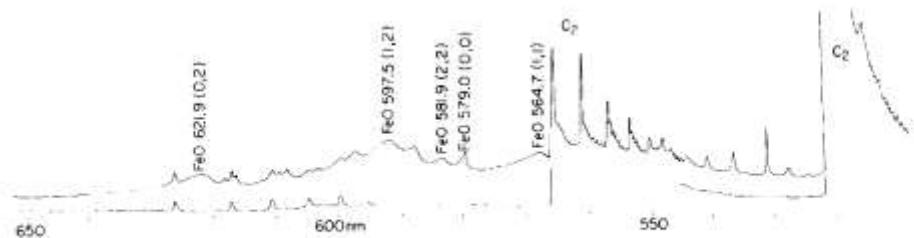


Fig. 5. Typical emission spectrum of FeO displayed on the oscillosgraph.

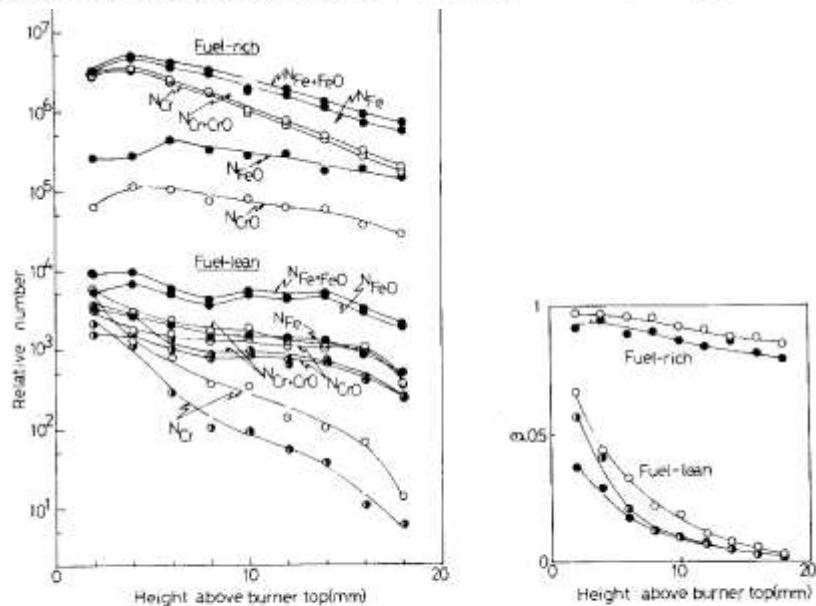


Fig. 8. Distribution of the relative number of species in fuel-rich and lean flames. The relative numbers of iron species are divided by the molar concentration ratio 20:80.
 (○) Cr(III); (★) Cr(VI); (●) Fe(III).

Fig. 9. Distribution of the β values. (○) Cr(III); (★) Cr(VI); (●) Fe(III).

K.Kitagawa , T.Takeuchi ,
 Analytica Chimica Acta ,
 Vol.60 , pp.309-318 (1972)

- ・<社会人時代>(昭和48 - 50年)
- ・日立製作所 那珂工場勤務: 旋盤工として半年の勤務を経て、保田和雄先生や小泉英明先生とZeeman原子吸光分析装置の開発や販売に従事した。水銀、直接分析のためにランプに磁場を印加し、サイドに分裂する α 成分をバックグラウンド吸光、変化しない π 成分を原子吸光に利用し、バックグラウンド補正を行った。後に、原子化器に磁場を印加する、逆ゼーマンへ展開した。(これは今なお販売されるヒット商品となるが、新規開発されない現状に嬉しくもあり悲しくもあり…)他に、開発部のトラブルターミネーターとして全国各地を回った。



図1 501型日立ゼーマン水銀分析計

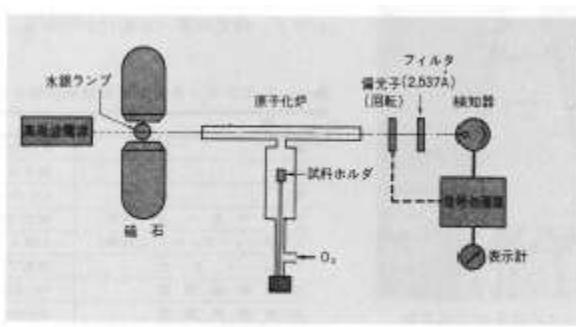


図2 501型
日立ゼーマン
水銀分析計構
造図



- 直接分析

Laser-assisted HF-heated cup glow discharge lamp for direct solid sample analysis

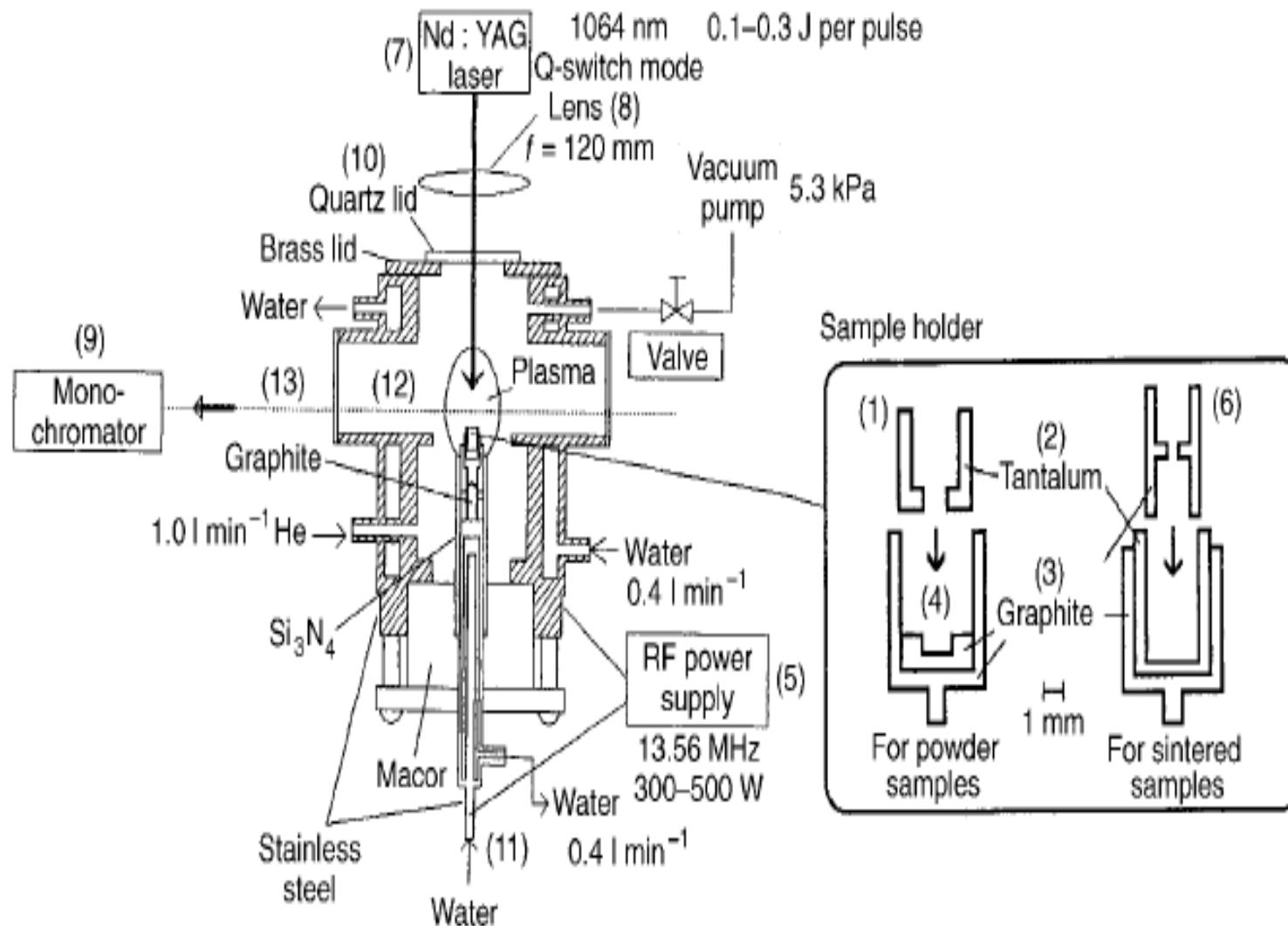


Fig. 1 Schematic diagram of the experimental system: (1) sample holder; (2) tantalum lid; (3) graphite cup; (4) graphite disk; (5) rf power source; (6) different type of sample holder for sintered ceramics; (7) Nd: YAG laser; (8) laser beam-focusing lens; (9) spectrometer; (10) quartz window for laser irradiation; (11) central electrode; (12) discharge chamber; and (13) quartz window for optical observation.

Table 1 Experimental conditions

Rf power	500 W (2100 °C),* or 350 W (1800 °C),† SWR = 1.5–3
Laser pulse	10 pulses s ⁻¹ , 124 mJ per pulse,* 270 mJ/pulse,† Q-switch mode
He pressure	5.3 kPa
He flow rate	1.0 l min ⁻¹ (NTP)
Bandpass of spectrometer	0.045 nm
Observation height	0–25 µm above the sample holder top
PMT voltage	–810 V (max.)
Flow rate of coolant water	0.4 l min ⁻¹

* For powdered samples.

† For sintered samples.

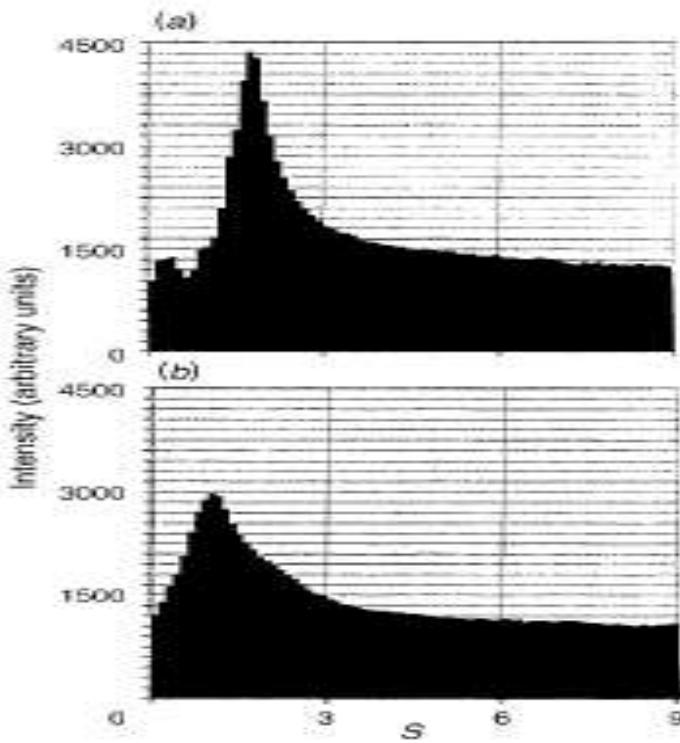


Fig. 2 Effect of laser irradiation on the emission peak in direct excitation of powder ceramics (a) with and (b) without laser irradiation. Sample, silicon nitride powder (SN-BL, Japan Fine Ceramics Center).

Table 2 Effect of laser irradiation on Al emission peak in direct excitation of powder ceramics ($n=4$). The sample and the conditions are the same as in Fig. 1.

	Without laser	With laser	Ratio
Average peak area (arbitrary units)	930*	1600	2.6
RSD (%)	5.1	2.8	0.55

* Sample powder residue was occasionally found in the cup. This value is based on 100% introduction.

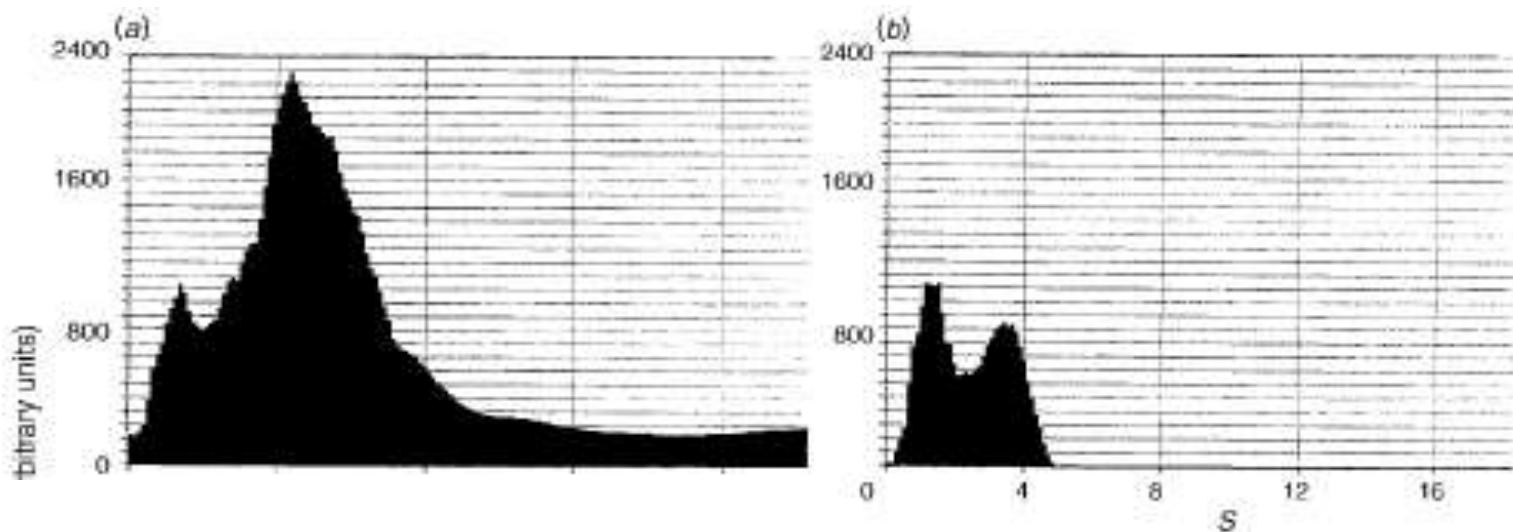


Fig. 3 Effect of laser irradiation on emission peak in direct excitation of sintered ceramics (a) with and (b) without laser irradiation. Sample, sintered silicon nitride (Japan Fine Ceramics Center) cut to about 1 mm³ (6–11 mg) with a diamond cutter. Wavelength = Mg I 279.553 nm.

Table 3 Effect of laser irradiation on Mg emission peak in direct excitation of sintered ceramics ($n=3$)

	Without laser	With laser	Ratio
Average peak area for 1 mg of the initial sample (arbitrary units)	1360	6660	4.9
RSD (%)	22.8	3.6	0.16
Average vaporized mass* (%)	17.7	43.6	2.5
Normalized peak area by ablated mass (arbitrary units)	7680	15300	2.0

* Calculated as 100(1 – residue mass/mass introduced).

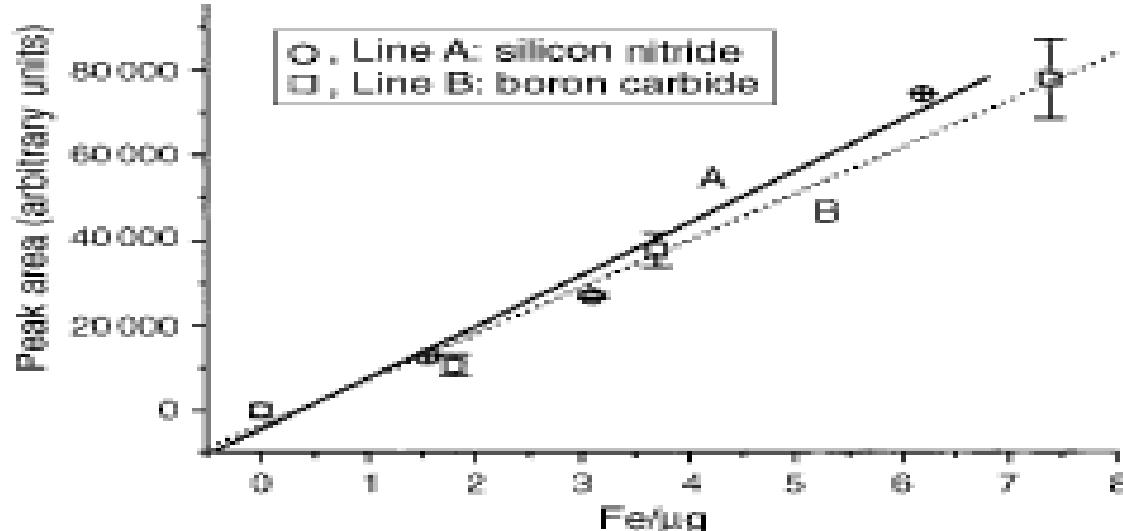


Fig. 4 Calibration curve for direct determination of Fe in silicon nitride using powder standards: ○ and A, with the powdered standard of silicon nitride; □ and B, with the powdered standard of boron carbide.

Table 4 Direct determination of Fe in sintered silicon nitride using powder standards ($n=3$). Wavelength = Fe II 259.940 nm*

	Powder standard	
	Silicon nitride	Boron carbide
Found (%)	0.039	0.042
Relative error (%) from the reference of 0.048%	23	14
RSD (%)	5.6	18

* The sample of sintered silicon nitride and standards are those available from the Japan Fine Ceramic Center.

直接分析のための分離原子化器

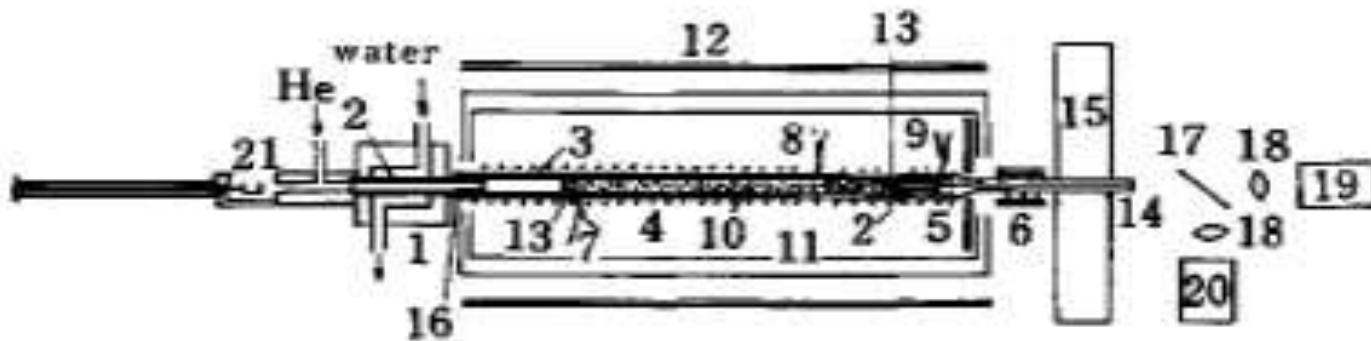


Fig. 1 Schematic diagram of the separative column atomizer/microwave-induced plasma system (SCA-MIP). condenser; 2, recrystallized alumina tube (4 mm i.d., 6 mm o.d.); 3, recrystallized alumina tube (6 mm i.d., 10 mm o.d.); 4, Kanthal wire heater 1; 5, Kanthal wire heater 2; 6, Kanthal

wire heater 3; 7, thermocouple (Pt/PtRh) 1; 8, thermocouple 2; 9, thermocouple 3; 10, activated charcoal (30–60 mesh); 11, ceramics case; 12, stainless steel case; 13, silica-alumina wool; 14, MIP discharge tube; 15, TM₀₁₀ microwave cavity;

wire heater 3; 7, thermocouple (Pt/PtRh) 1; 8, thermocouple 2; 9, thermocouple 3; 10, activated charcoal (30–60 mesh); 11, ceramics case; 12, stainless steel case; 13, silica-alumina wool; 14, MIP discharge tube; 15, TM₀₁₀ microwave cavity;

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Table 1 Equipment

Spectrometer

Nippon Jarrell-Ash Model JE-50E, $f=0.5$ m
photomultiplier tube HTV R666

Jobin-Yvon Model H20UV, $f=0.2$ m, photomultiplier
tube R763

Photomultiplier tube power supply

Laboratory-made

Microwave power supply

Electromedical Supply Model Microtron 200 MK-2

Microwave cavity

Laboratory-made silver-plated brass TM₀₁₀ type
(92 mm i.d., 122 mm o.d., 15 mm height and 8
mm hole)

X-Ray fluorescence analyzer

Kevex/Rigaku Model Untratrace System 0600

Strip chart recorder

Toa Denpa Model FBR-251A and 252A

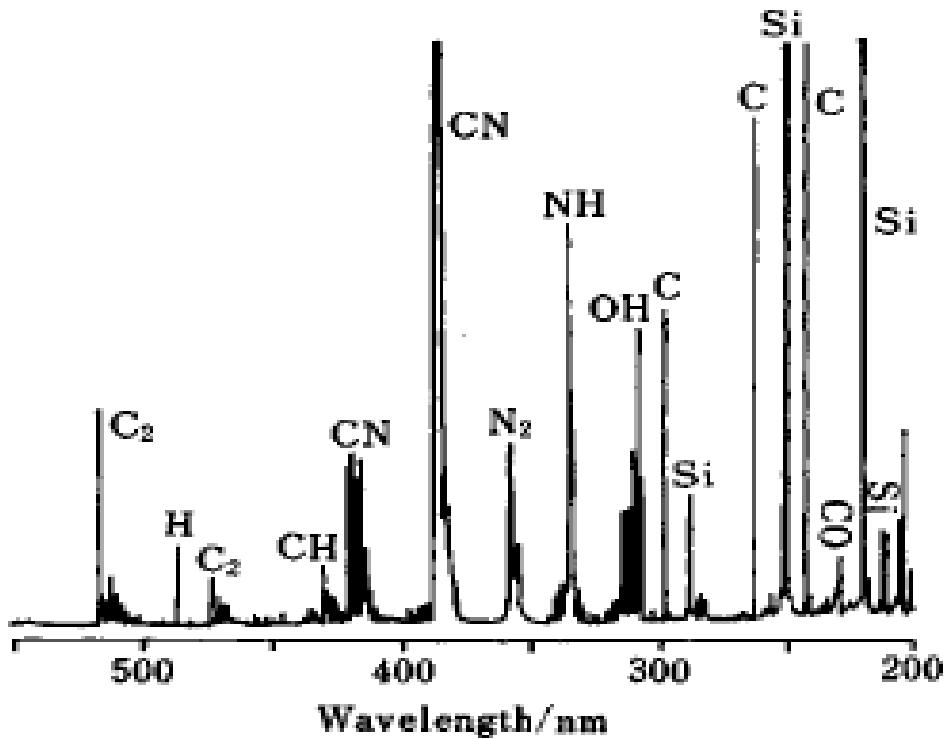


Fig. 2 Background emission spectrum from the SCA-MIP system. Discharge tube, fused silica tube (2 mm i.d., 4 mm o.d.) cooled with air; microwave power, 80 W incident and 5 W reflected; He carrier, 100 ml min⁻¹ STP.

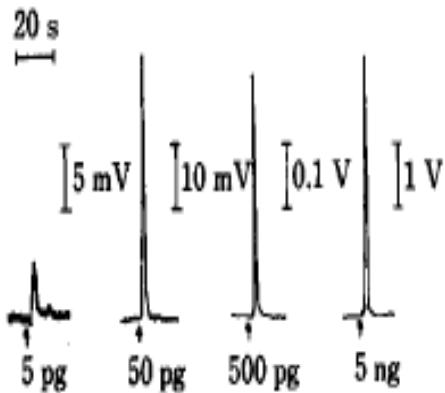


Fig. 3 Typical signal traces of Hg emission. Sample, 5 μ l of $\text{HgCl}_2/0.5\%\text{EDTA}\cdot2\text{NH}_4$; wavelength, 253.65 nm; column temperature, 1100°C (column middle); arrows, sample introduction.

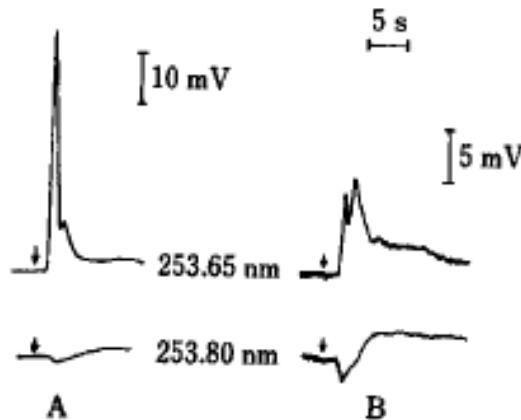


Fig. 4 Typical signal traces of Hg emission with solid samples. A, NBS Orchard Leaves SRM 1571 0.64 mg in 5 μ l suspension; B, Bovine Liver SRM 1577 0.68 mg in 5 μ l suspension; SCA condition, same as in Fig. 3.

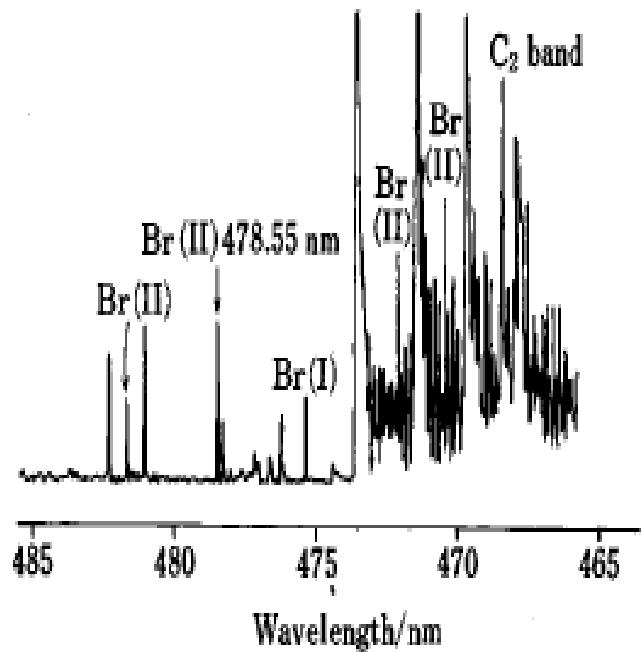


Fig. 5 Emission spectrum of Br from the SCA-MIP. Sample, bromobenzene saturated in the He carrier; SCA condition, same as in Fig. 3.

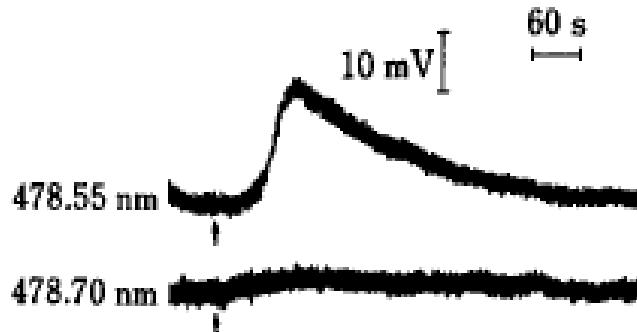


Fig. 7 Typical signal traces of Br and background emissions. Column temperature, 1280°C (column middle); He carrier, 100 ml min⁻¹ STP; sample 20 µg Br (5 µl) as NH₄Br.

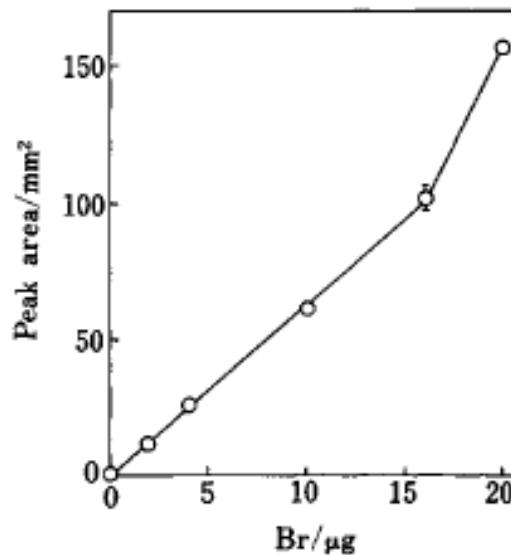


Fig. 8 Calibration curve of Br. Sample, 5 µl as NH₄Br; He carrier, 400 ml min⁻¹ STP; column temperature, same as in Fig. 7.

直接分析のための原子磁気旋光分光法

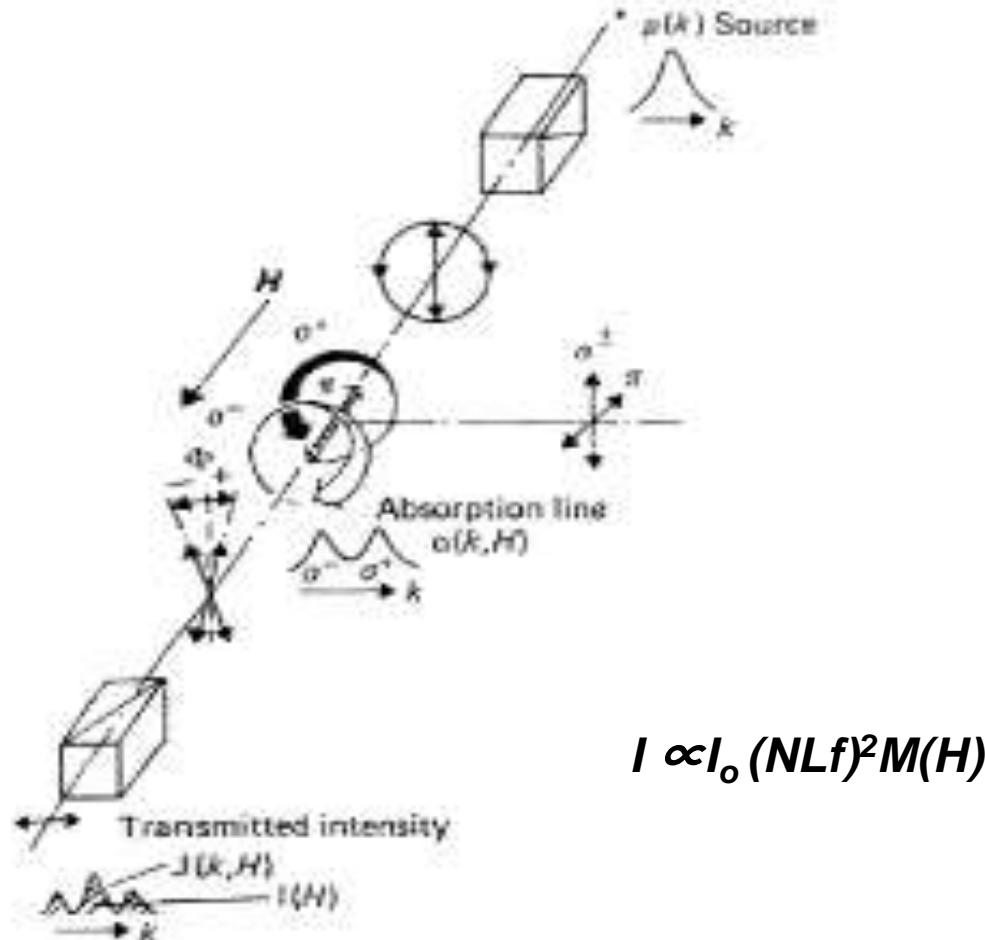


Fig. 2. Relation between the Faraday effect
and the Zeeman effect.

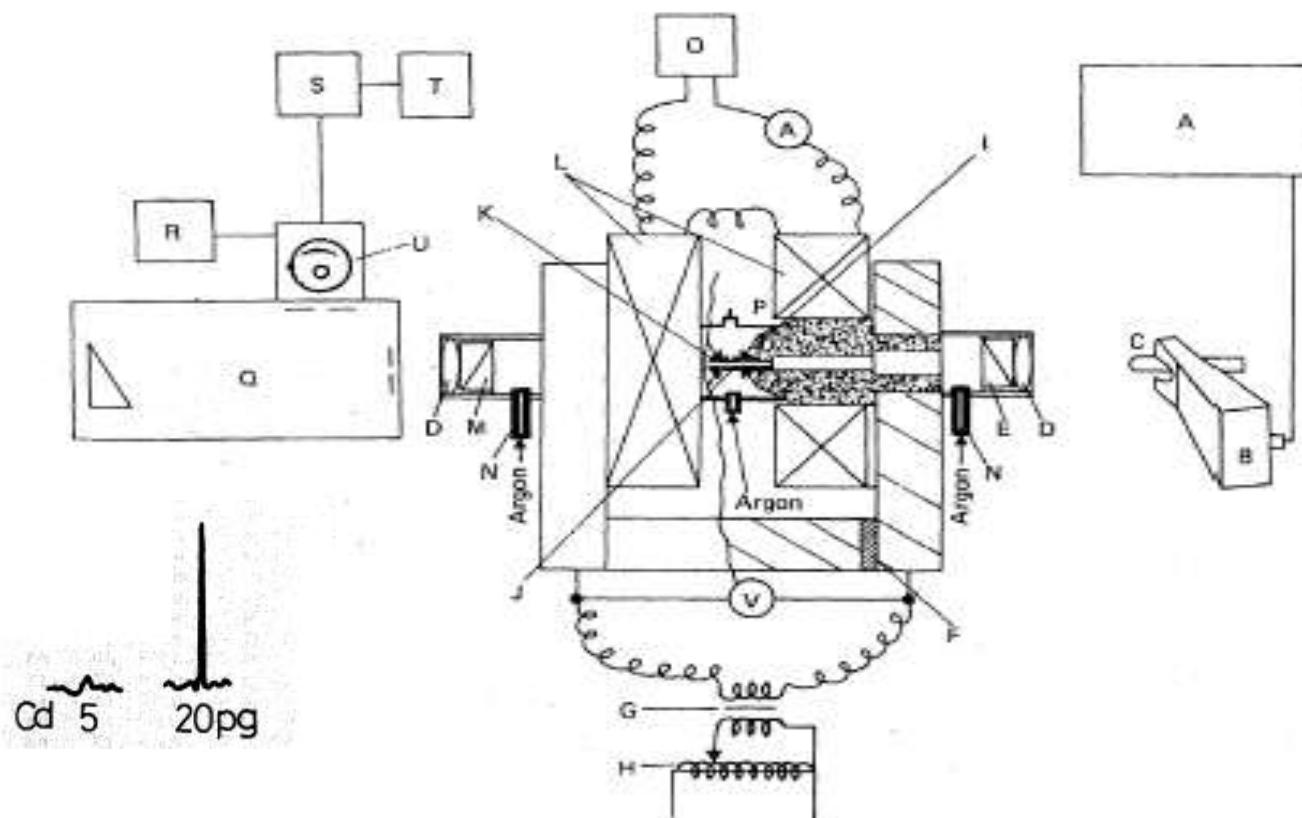


Fig. 4. Schematic diagram of the optical system: A, microwave power supply for the electrodeless discharge lamp; B, microwave cavity; C, electrodeless discharge lamp; D, lens; E, polarizer; F, insulator; G, transformer; H, variable transformer; I, pole piece; J, graphite tube atomizer; K, graphite cone; L, solenoid coil; M, analyzer; N, gas inlet; O, power supply for the solenoid coil; P, chamber; Q, prism monochromator; R, stabilizer for high-voltage supply for the photomultiplier tube; S, d.c. amplifier; T, strip-chart recorder; and U, photomultiplier tube.

$$\text{吸光の補正 } I_{\text{corr}} = I_{\text{amor}} / I_{\text{aas+bga}}$$

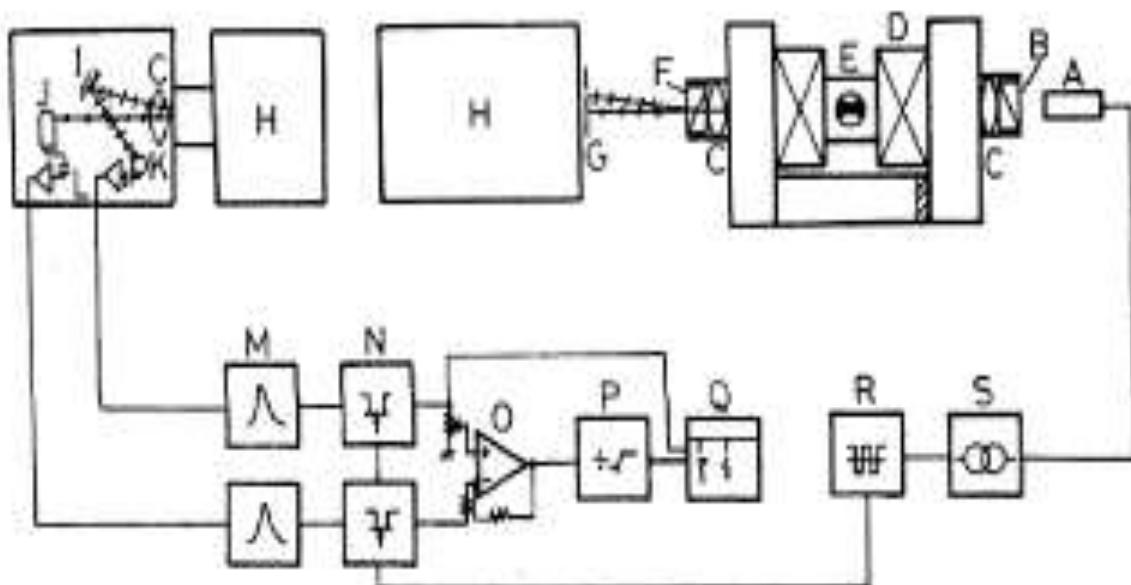


Fig. 8. Schematic diagram of the experimental arrangement. (A) hollow cathode lamp, (B) Glen-type prism, (C) lens, (D) electromagnet, (E) graphite tube atomizer and atomization chamber, (F) Rochon prism, (G) iris diaphragm, (H) prism monochromator, (I) plane mirror, (J) photomultiplier tube (R955), (K) photomultiplier tube (R306), (L) a.c. preamplifier, (M) bandpass filter amplifier, (N) phase-sensitive rectifier, (O) off-set amplifier, (P) operational amplifier for dividing and square root processing, (Q) strip chart recorder, (R) pulse generator and (S) current stabilizing power supply.

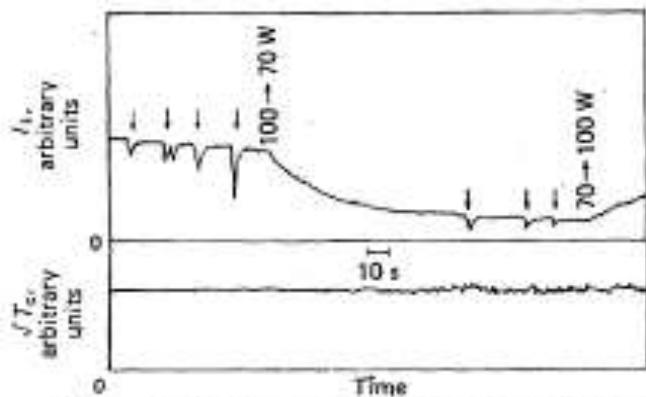


Fig. 9. Traces showing correction for energy loss and variation in intensity of source radiation. Arrows indicate the introduction of cigarette smoke.

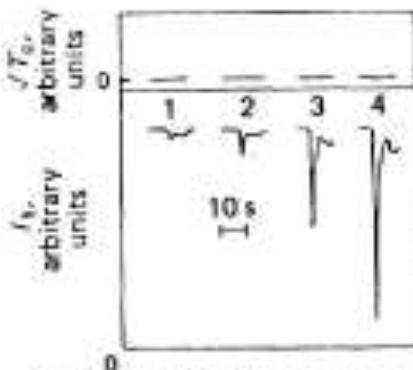


Fig. 10. Oscilloscope traces of the corrected response for pyrolysis of different amounts of starch at the atomization temperature of 1800 °C, showing the background scattering. 1, No starch; 2, 2.5 µg of starch; 3, 5 µg of starch; and 4, 10 µg of starch.

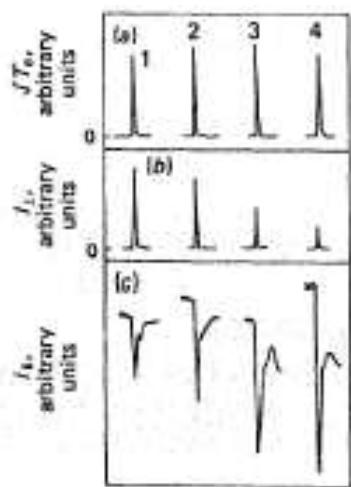


Fig. 11. Correction of energy loss and variation in intensity of source radiation for electro-thermal atomization. 1, 50 µg of cadmium; 2, 5 µg of starch added; 3, 10 µg of starch added; and 4, 15 µg of starch added. See text for explanation of (a), (b) and (c).

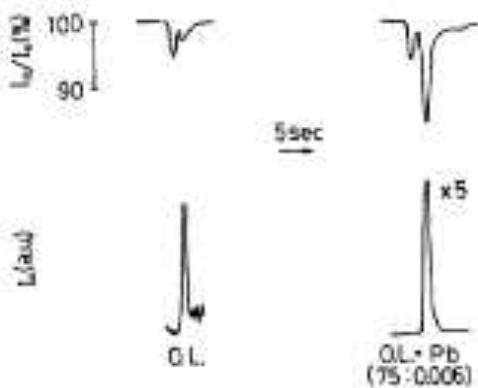


Fig. 12. Typical peaks of I_1 and I_0 for NBS Orchard Leaves SRM 1571. O.L. = Orchard Leaves.

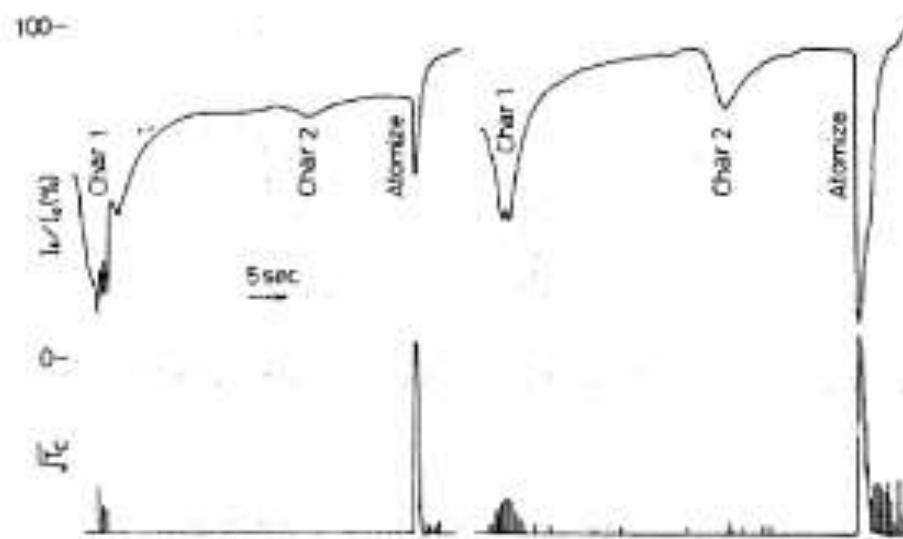


Fig. 14. Two typical cases of correction in the analysis of human blood.

Table 1. Results of analysis

Element	Sample	Found*		Certificate or reference
		S.A.M.	C.M.	
Pb	NBS			
	Orchard			
	Leaves			
	SRM 1571			
	(ppm)	45.3 ± 0.9		45 ± 3
	Human	1	106 ± 19	90†
	Blood	2	100 ± 16	110†
	(in g dl^{-1})	3	144 ± 19	140†
Volcanic		1	3.5 ± 0.7‡	
	ashes (ppm)	2	4.3 ± 0.7§	
		3		5
Mn	Volcanic ashes (%)		0.069 ± 0.007	0.07
Cr	Orchard	(350°C)	2.4 ± 0.5	
	Leaves (ppm)	(700°C)	2.3 ± 0.4	2.6 ± 0.3
	Volcanic ashes (ppm)	1	28 ± 10‡	
		2	34 ± 5§	29§

* Results based on at least five replicate determinations.

† Taken from normal persons in December, 1979 and analysed in Public Health Research Laboratory, Medical School, Nagoya City University, Mizubokawasumi, Mizuho-ku, Nagoya, Japan.

‡ Taken near the 8th station of Ontake Volcano in November, 1979.

§ Taken in Kaido Village, Nagano, Japan, in November, 1979.

|| Taken in Shinbashi, Nagano, Japan, in November, 1979 and analysed in Nagano Research Institute for Health and Pollution, Kome-mura, Oaza-Amori, Nagano, Japan.

S.A.M. = Standard Addition Method.

C.M. = Calibration Method.

Precisions given in terms of S.D.

Temperatures in parentheses are charring temperature.



車載用小型原子磁
77.3.11一配置)¹¹⁾

mbysis



Fig. 3. The first and second authors holding the cylinder and the constructed AMORS, respectively, the two car batteries and a second author's motor car (Mitsubishi Lancer) to carry them

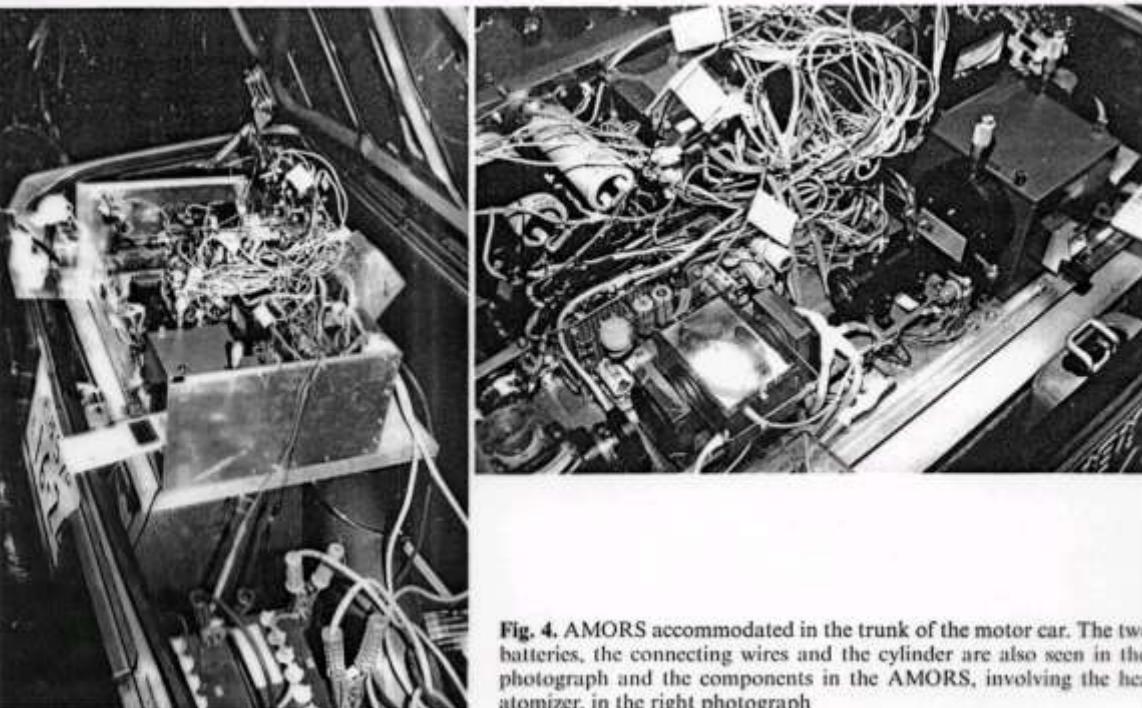


Fig. 4. AMORS accommodated in the trunk of the motor car. The two batteries, the connecting wires and the cylinder are also seen in the photograph and the components in the AMORS, involving the heat atomizer, in the right photograph

the car batteries and the cylinder accommodate of the motor car. Wires connecting the batti AMORS are to be seen. When used, the connected in series to generate 24 V. Two fur connected in a parallel are mounted in the er the motor car and charged during car runn pairs of the car batteries are alternately chargeec car and discharged by the AMORS.

2.2 Electronic System

Figures 5 and 6 show the block diagram of system constructed and the relevant time c sequences produced by timing circuits, resp photocurrents from the photomultiplier tube $\frac{1}{2}$ inch compact type) are amplified and co corresponding voltages by the preamplifier amplifier IC Intersil LF356) and sent to the f circuits.

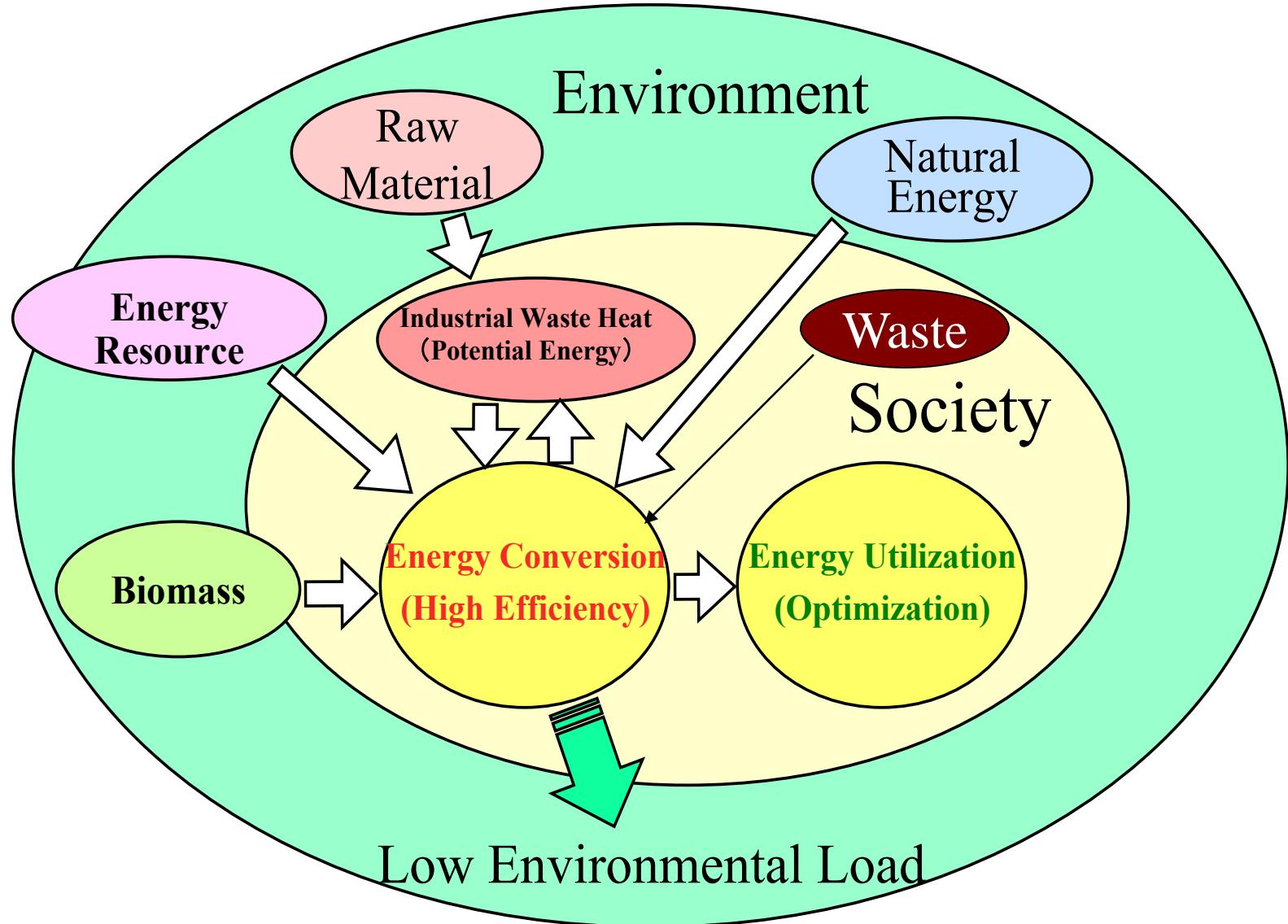
During a short period when a hole on the c intersecting the optical axis, a blank volta sponding to the photocurrents induced by f

- ・<助手・講師時代>(昭和50 - 平成6年)竹内次夫先生、柘植 新先生、柳沢正明先生、Horlick先生らと原子分光分析法研究

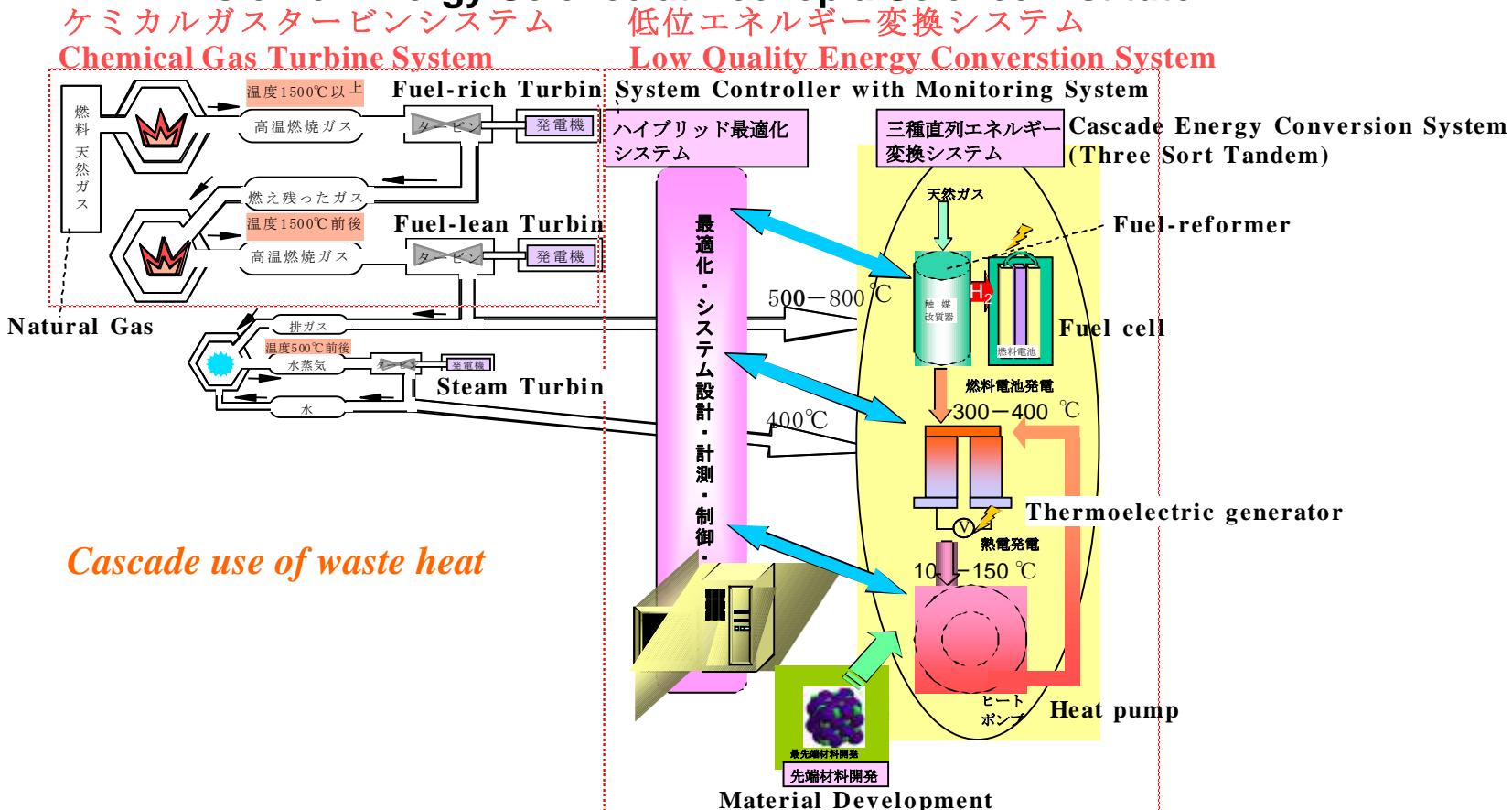
*1983年日本分析化学会奨励賞(楠先生、中村先生と)



Institute of Energy Science



名古屋大学旧高効率エネルギー変換研究センター
 Research Center for Advanced Energy Conversion, Nagoya University (RAN)
Division of Energy Science at EcoTopia Science Institute





Advanced Energy Conversion Group

Division of Energy Science

EcoTopia Science Institute

Nagoya University

- Prof. Kiatagwa, Assist. Prof. Morita, Dr.Matsumoto & Dr. Nelfa
 - Spectroscopic analyses of combustion, Fuel cell, Hydrothermal reforming of biomass and biowaste, LED illumination
- Assoc. Prof. Takashi Itoh
 - Syntheses and systems of thermoelectric materials
- Prof. Yutaka Hasegawa
 - Turbine compressor and wind turbine systems

Assoc. Prof. Kojima

Chemical gas turbine, combustion systems and supersonic fuel reforming

Prof. Kobayashi & Dr. Huan

Heat pump systems and CO₂ issues

Chemicalgas turbine system

Study of combination of fuel-rich and fuel-lean combustions using a two-step gas turbine

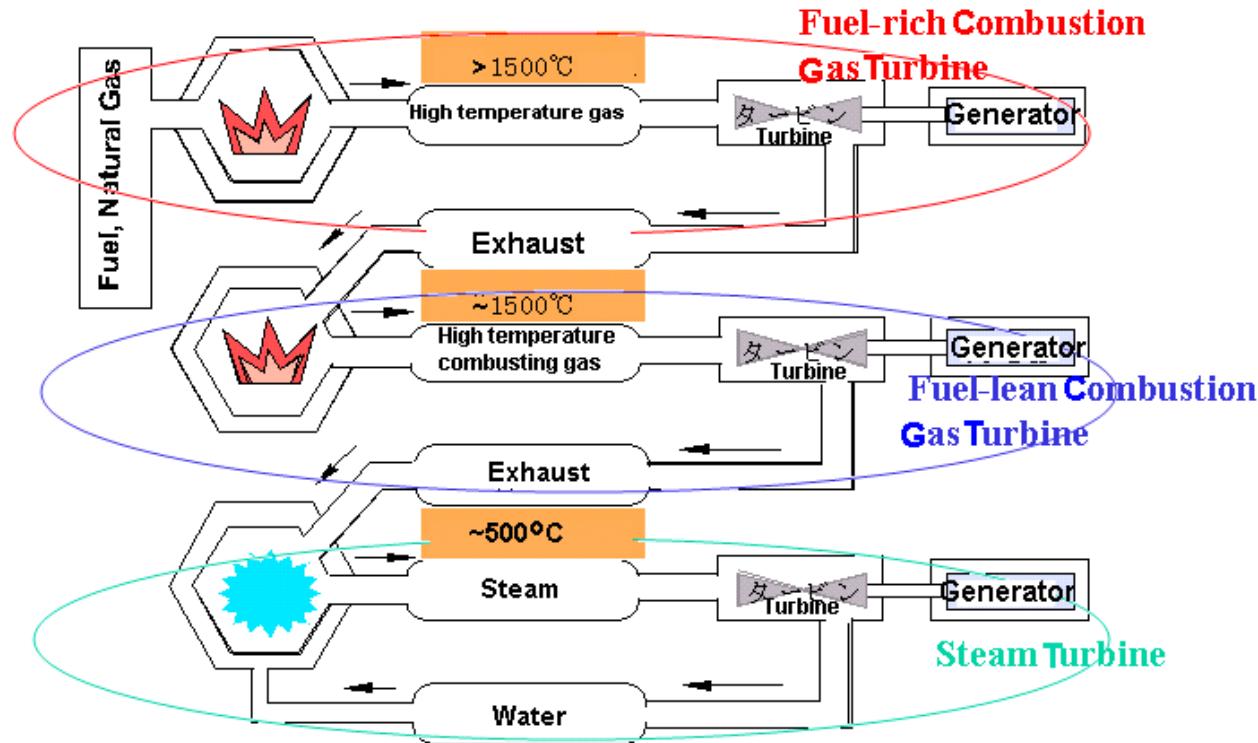


Fig. Illustration of a chemical gas turbine system

Fuel-rich Combustion Gas Turbine



- Low NOx Emission from Regenerative Industrial Furnace for kira-kira 30% Energy Saving
- Spectroscopic Observation

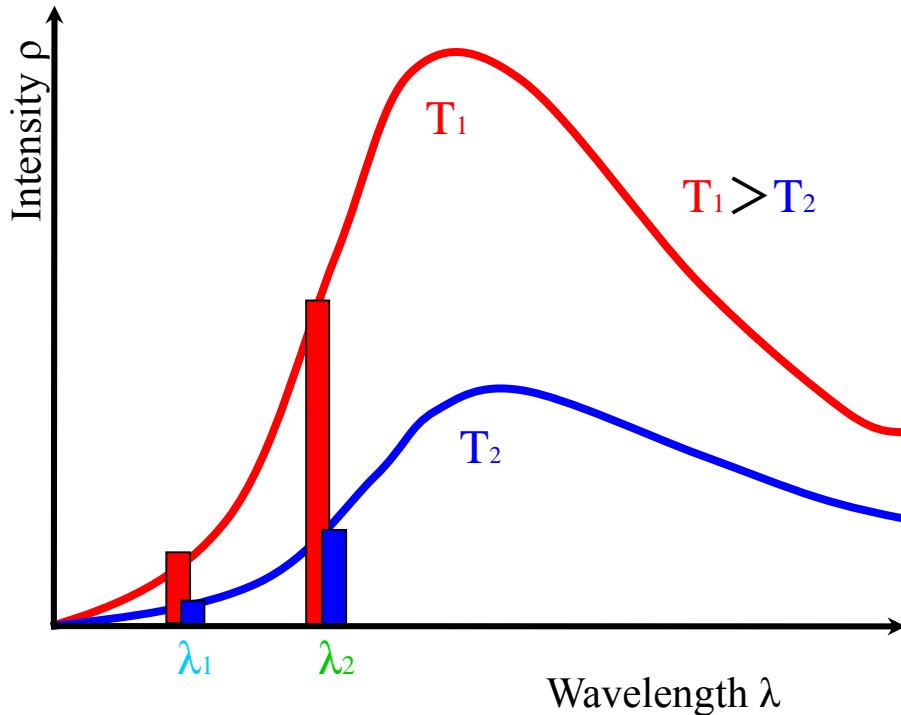
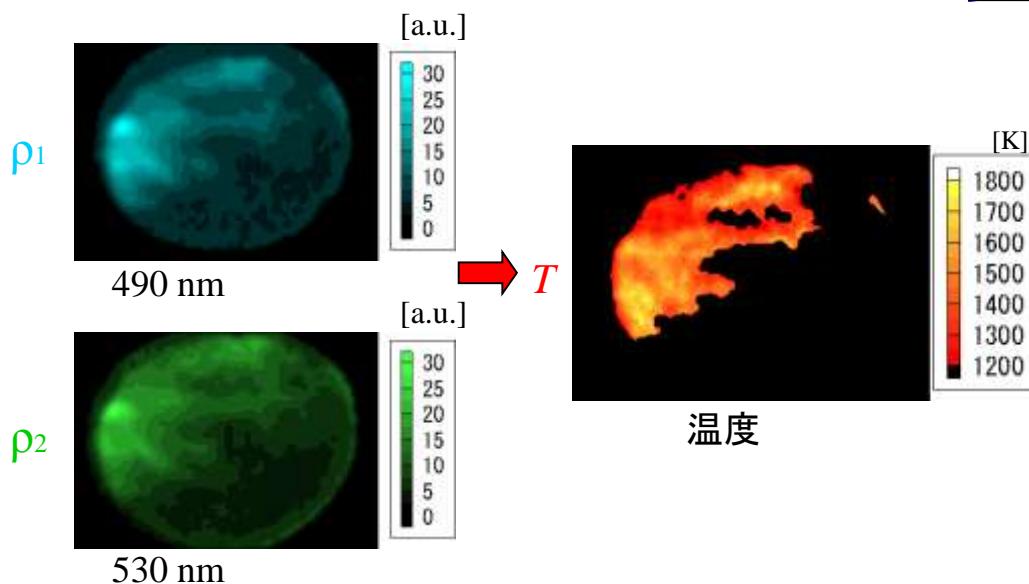
Two-color method

Planck's law

$$\rho = \varepsilon_\lambda \cdot \frac{8\pi hc}{\lambda^5} \cdot \frac{1}{\exp(hc/\lambda kT) - 1}$$

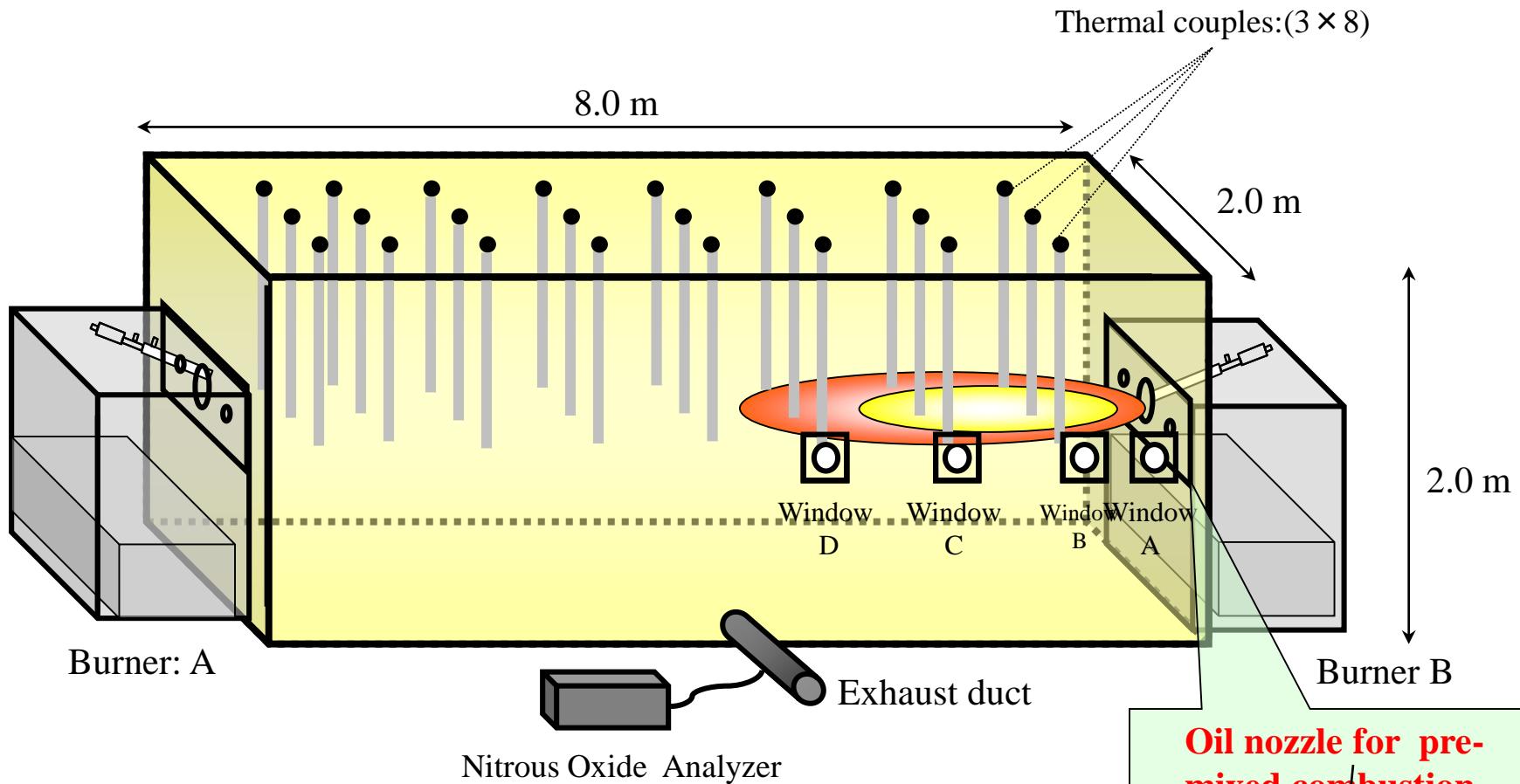
Taking a ratio of intensities at 2 wavelengths,

$$\frac{\rho_2}{\rho_1} = \left(\frac{\lambda_1}{\lambda_2} \right)^5 \cdot \frac{\exp(hc/\lambda_1 kT) - 1}{\exp(hc/\lambda_2 kT) - 1}$$



ρ :	Unit radiation energy $[Jm^{-4}]$
h :	Planck's const $6.62608 \times 10^{-34} [Js]$
λ :	Wavelength $[m]$
c :	light velocity $2.99792458 \times 10^8 [ms^{-1}]$
k :	Boltzmann const $1.38066 \times 10^{-23} [JK^{-1}]$
T :	Temperature $[K]$
ε_λ :	Emissivity [-]

Object :Test Furnace of Keihin Iron Plant, NKK (Currently JFE)



Fuel :Heavy Oil

Combustion:

Pre-mixed combustion : combustion of fully mixed air and fuel takes place in the chamber

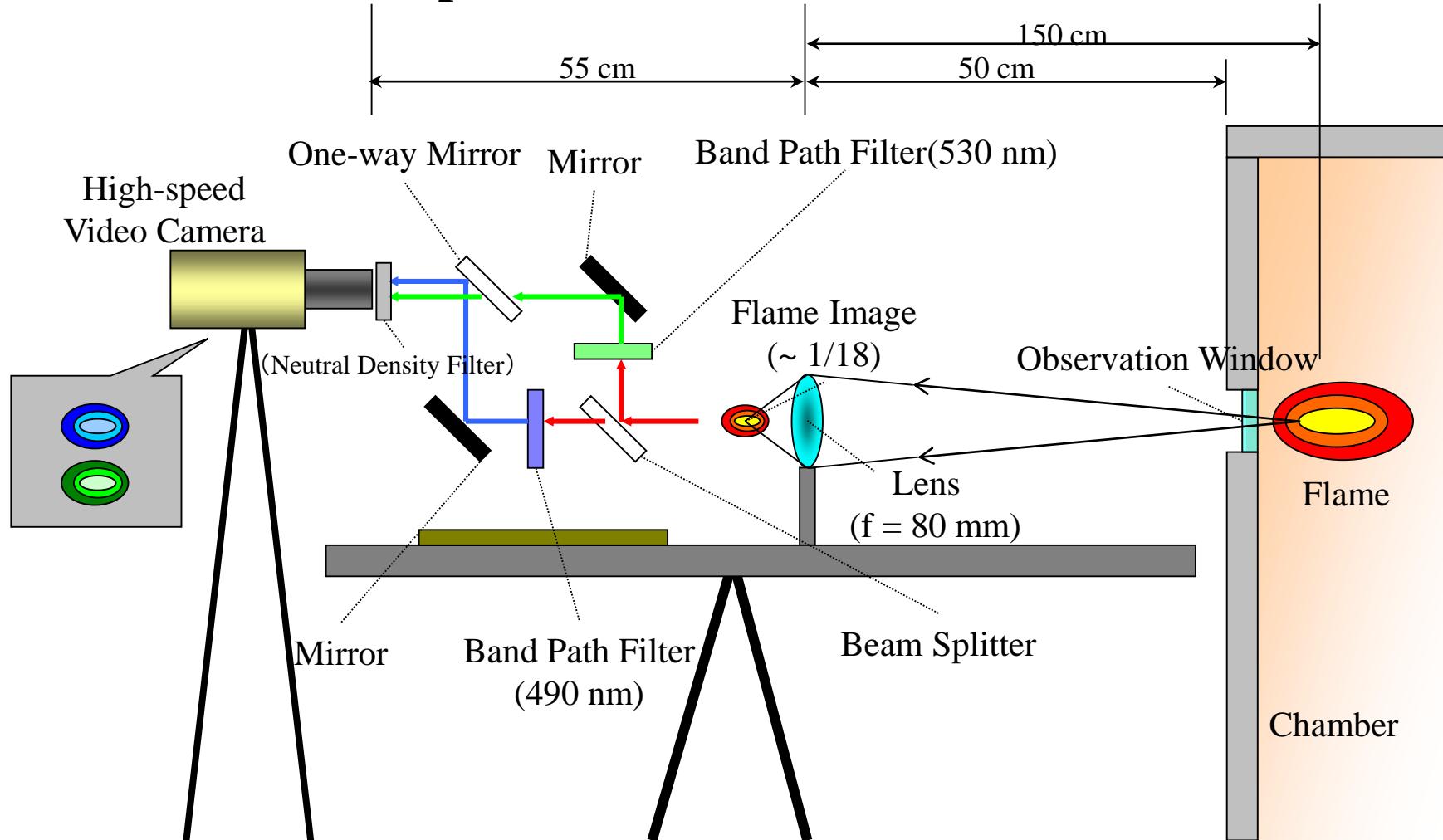
Diffusion combustion : Combustion and mix of fuel and air takes place at the same time in the chamber

Oil nozzle for pre-mixed combustion



Oil nozzle for diffusion combustion

Measurement Set-up



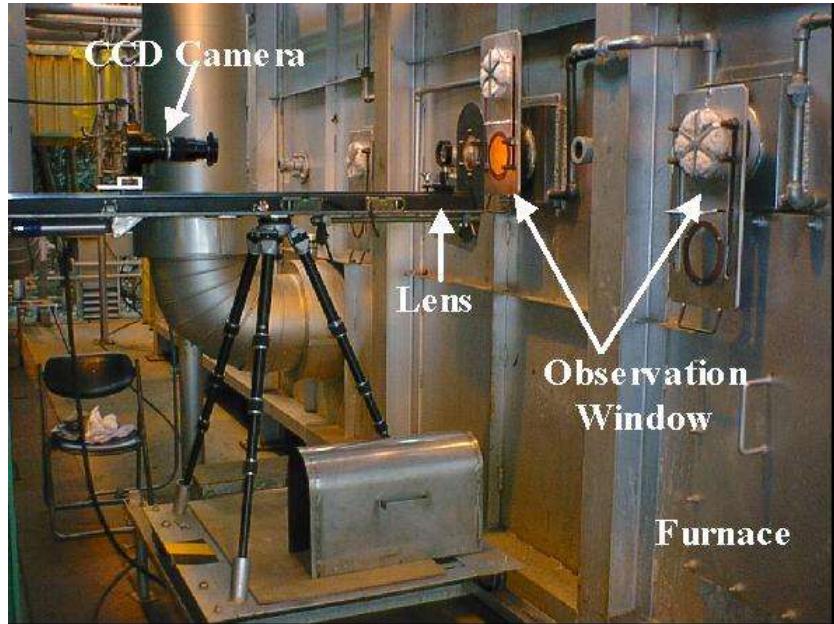
Band Path Filter:

530.88 nm(Half Width 8.77 nm)

490.0 nm (Half Width 28.0 nm)

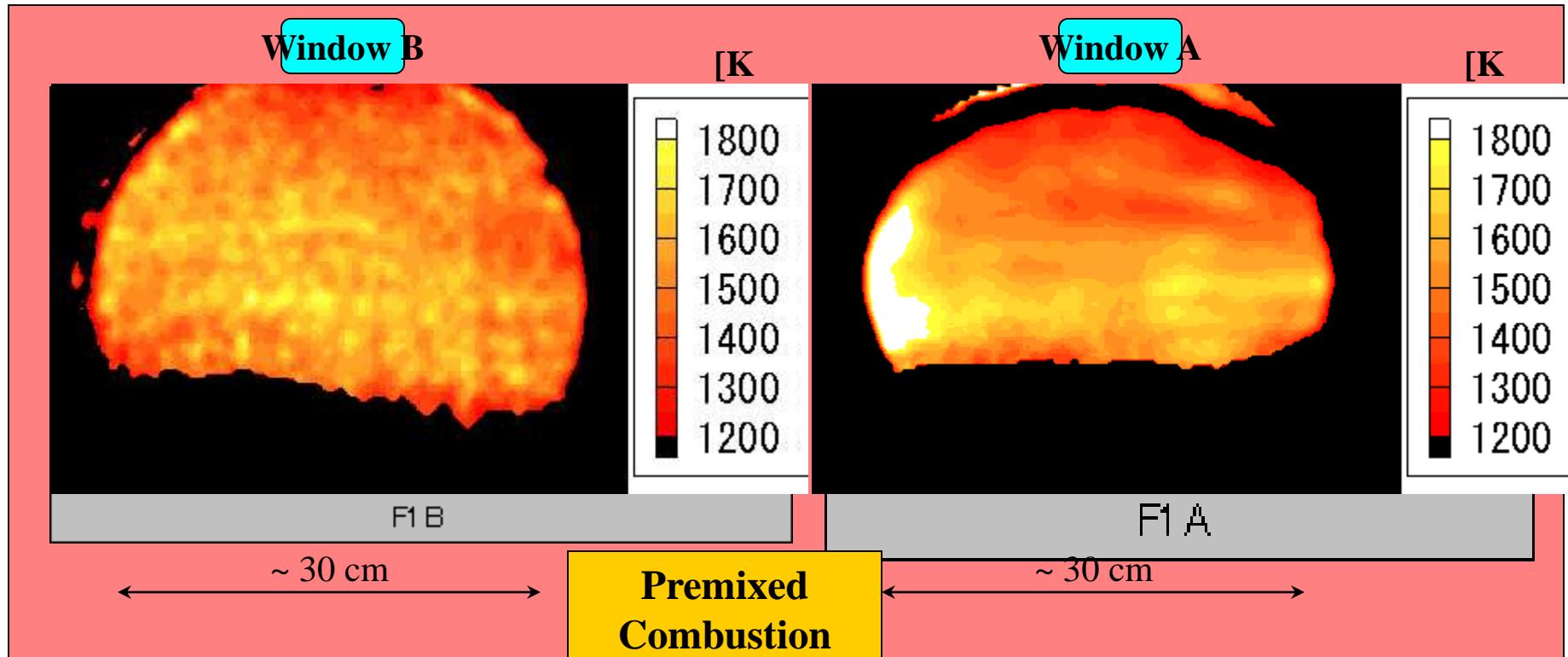
High-speed video camera (photron,FASTCAM ultima 40K)

Top Speed: 125 frame/sec Exposure Time: 1/125 sec

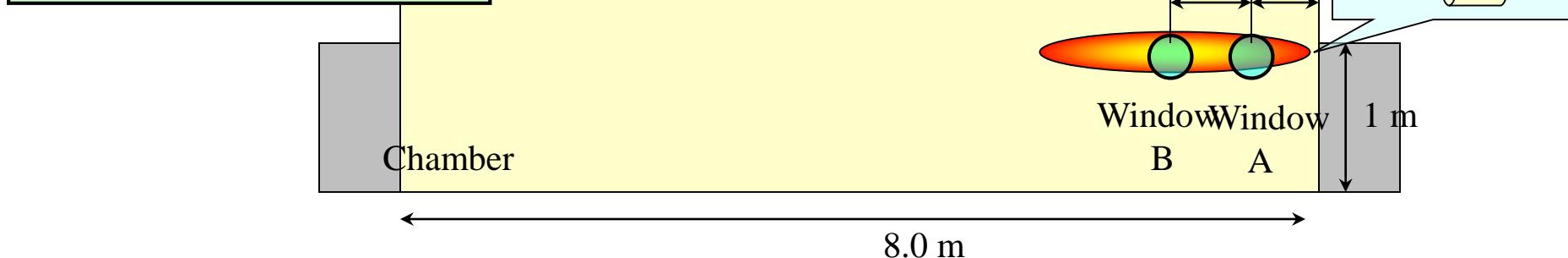


Temperature profiles (premixed combustion)

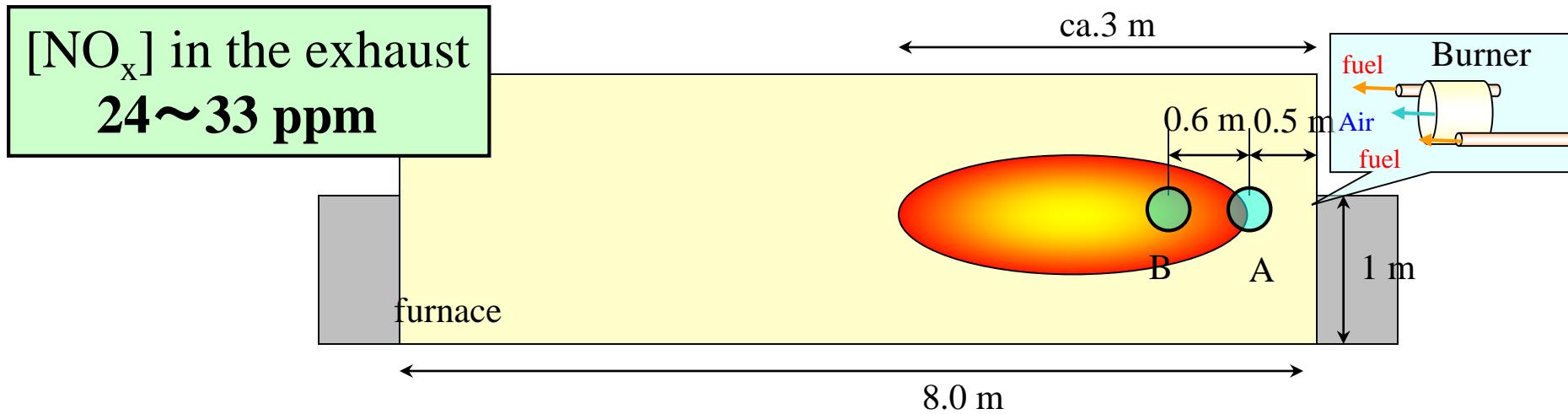
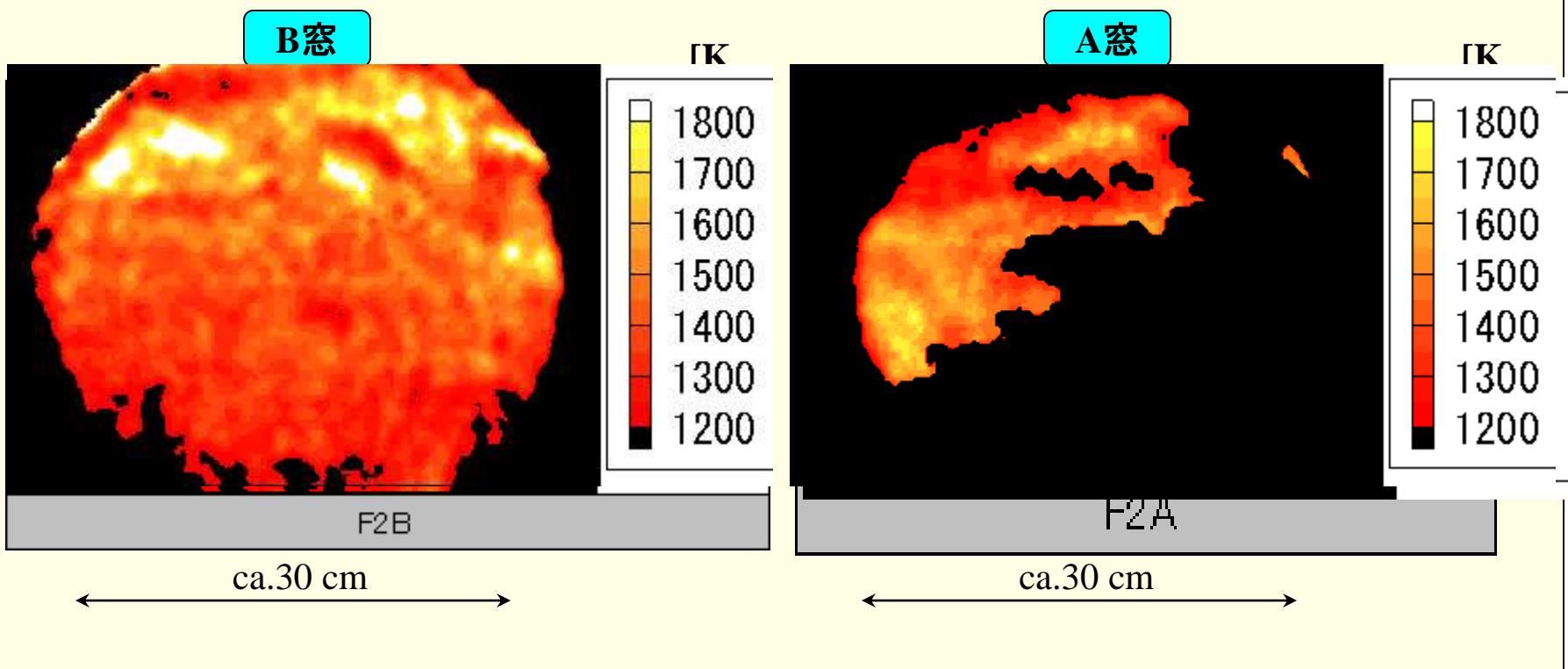
(Slow Motion(~1/10))

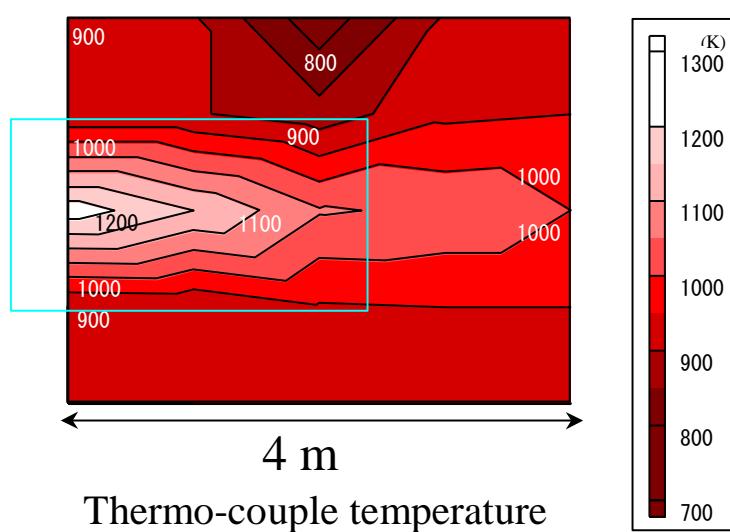


[NO_x] in the exhaust
126~144 ppm

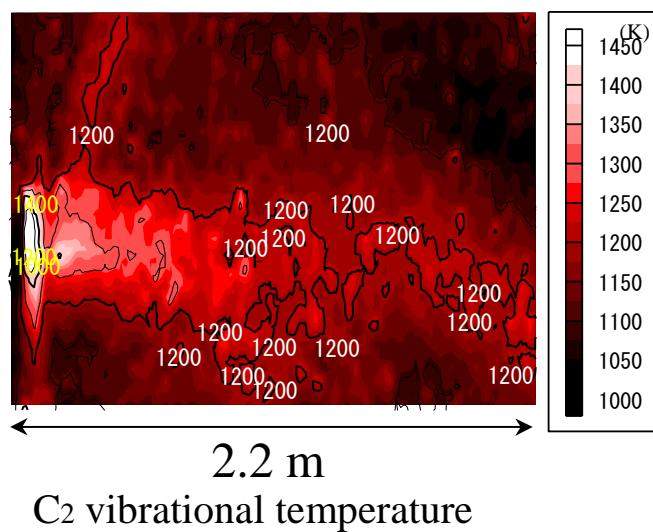


Temperature profiles (diffusion combustion)





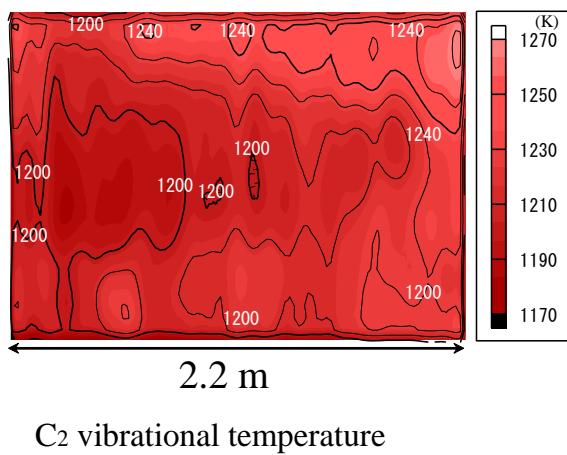
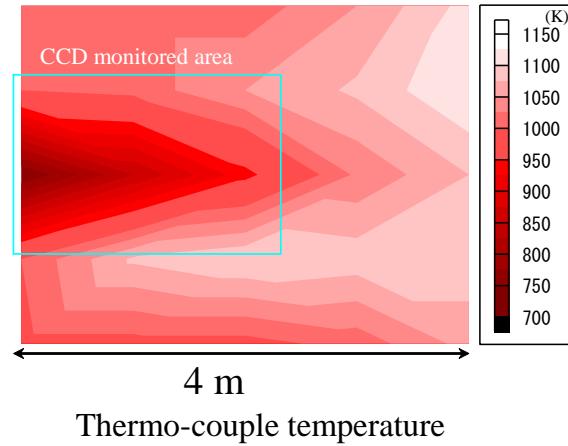
Thermo-couple temperature



C₂ vibrational temperature

Premixed flame Exposure time 0.01[s]

Figure 5 Temperature distribution



Diffusion flame Exposure time 0.01[s]

Figure 4 Temperature distribution

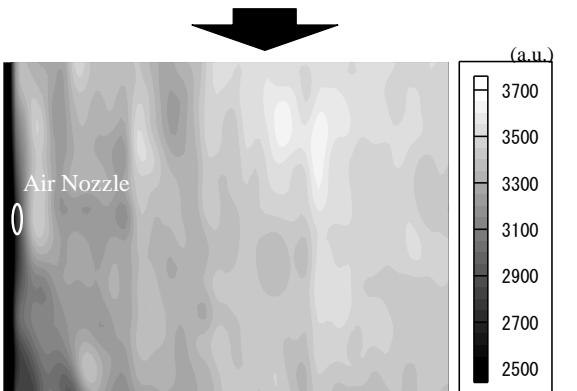
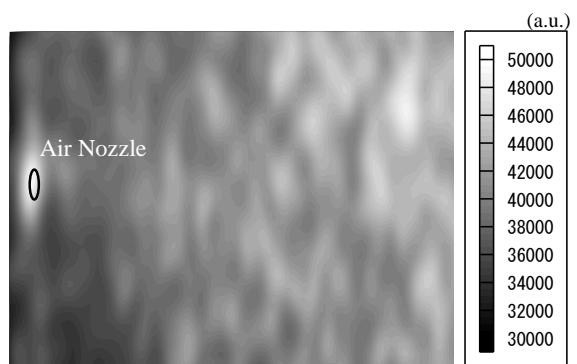
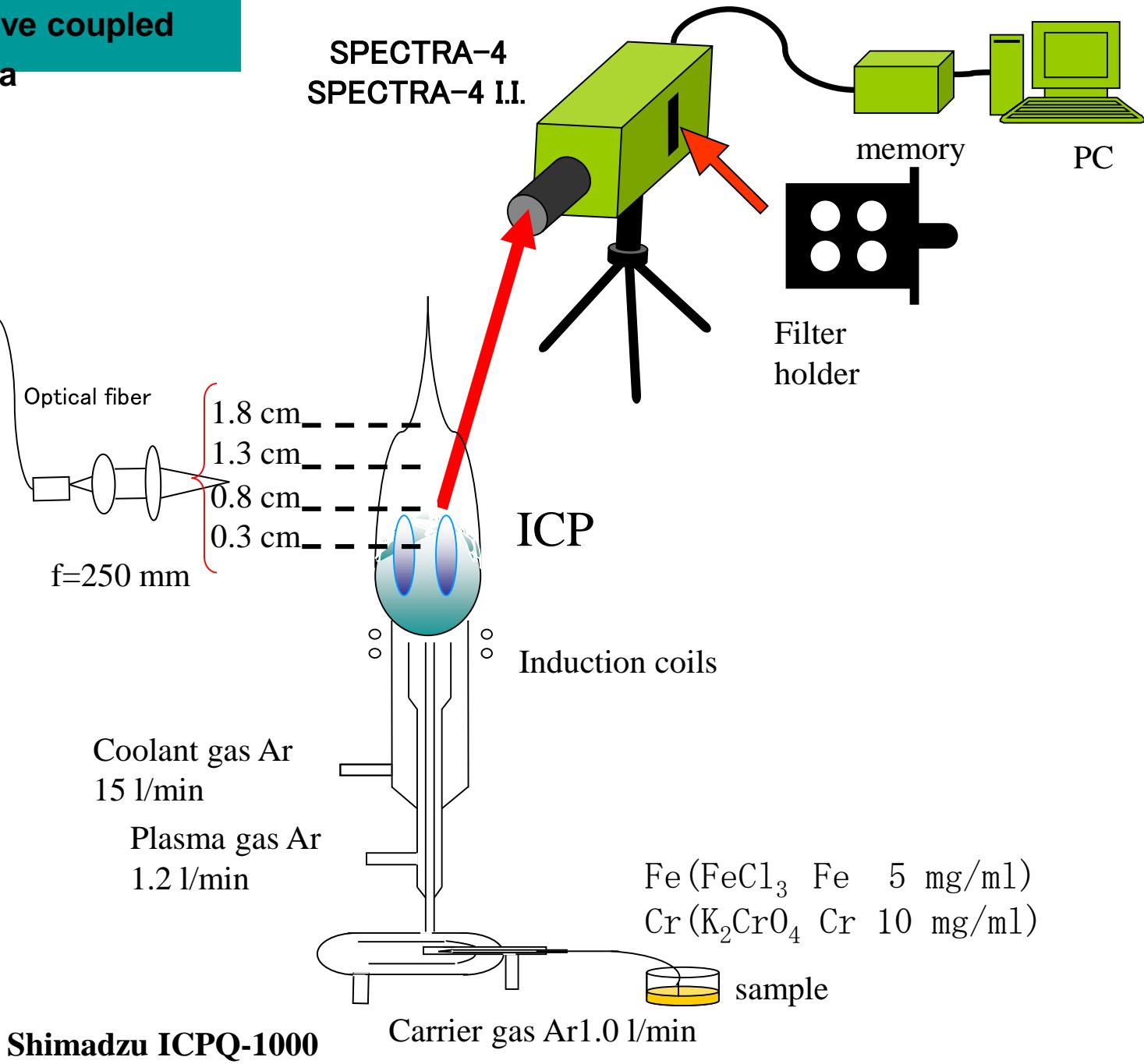
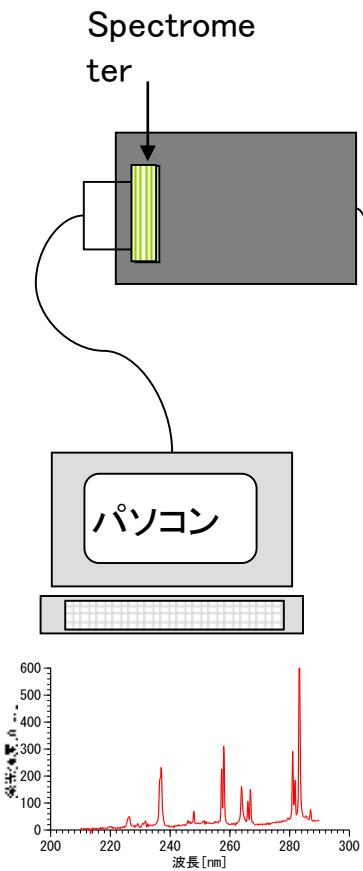


Figure 8 NO Emission Intensity

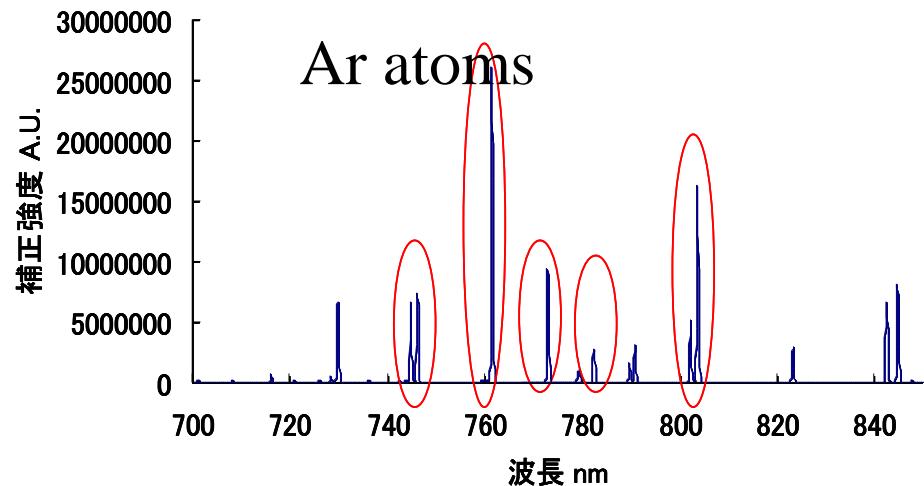
ICP

Inductive coupled plasma

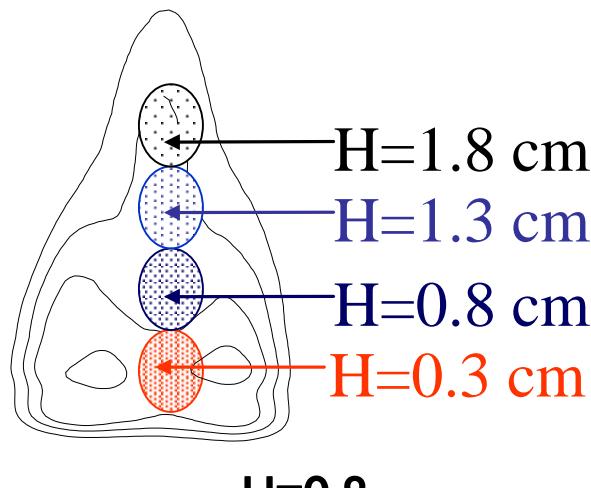
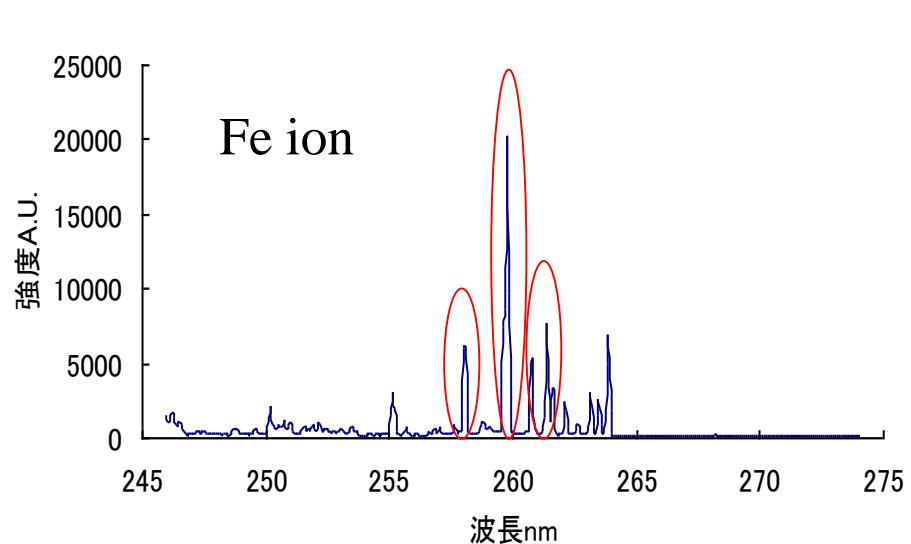


Excitation temperature

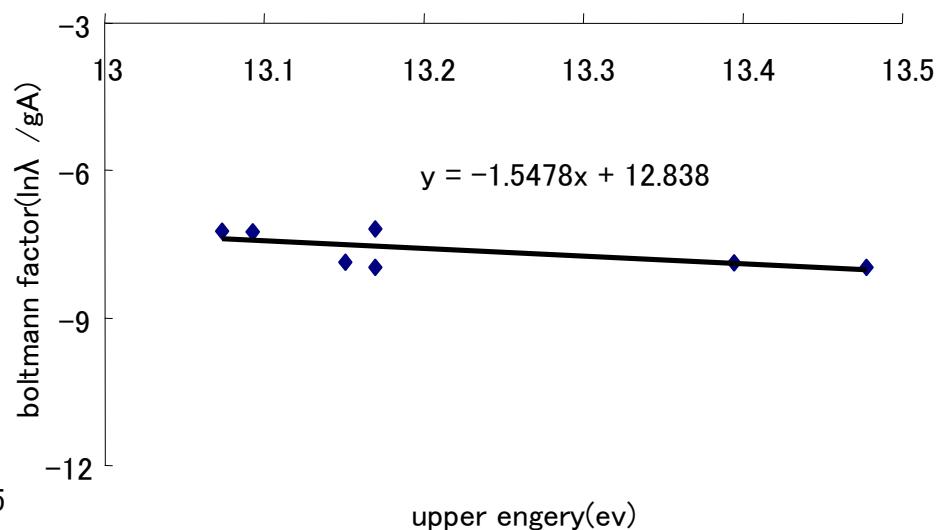
H=0.8cmICPプラズマの発光スペクトル

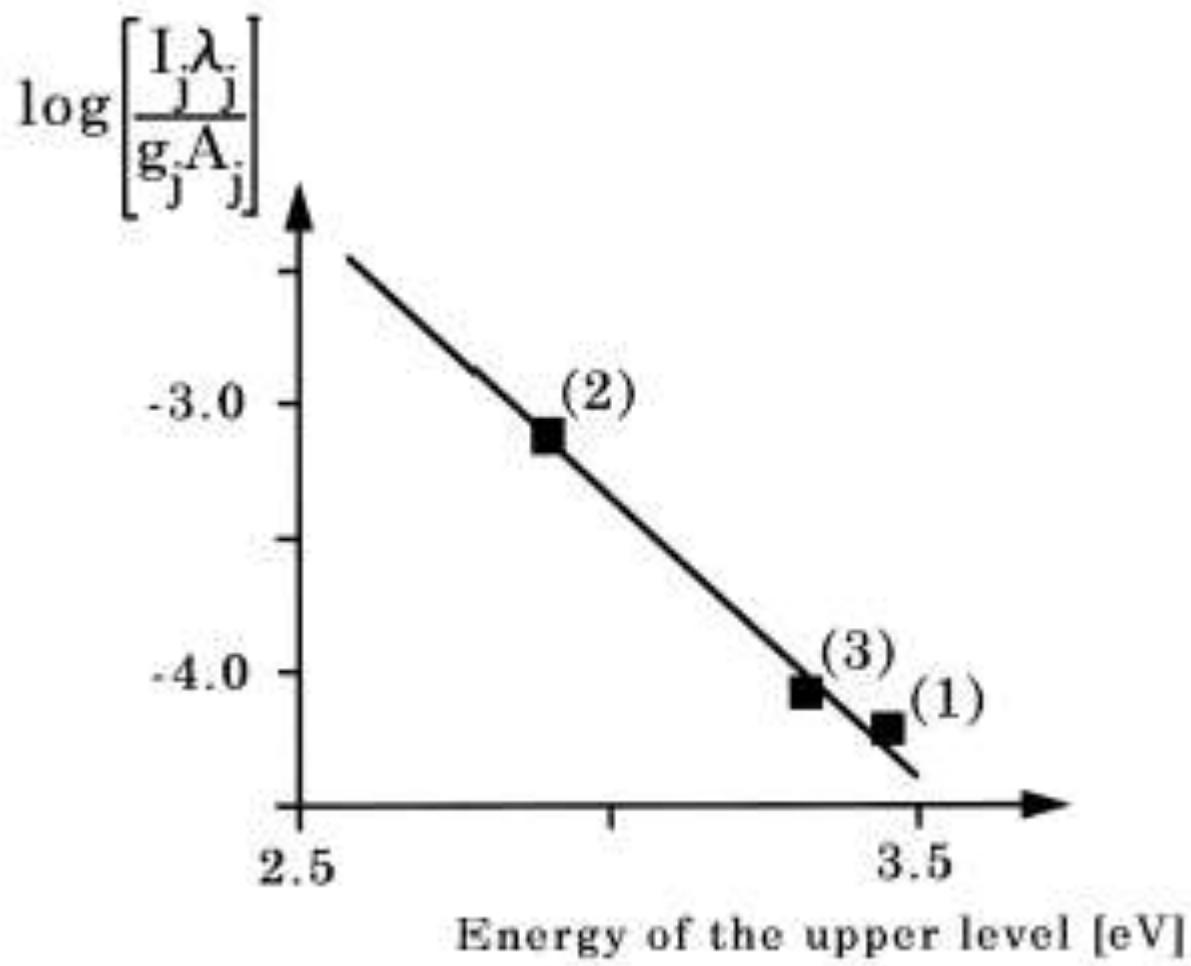


H=0.8cmICPプラズマの発光スペクトル

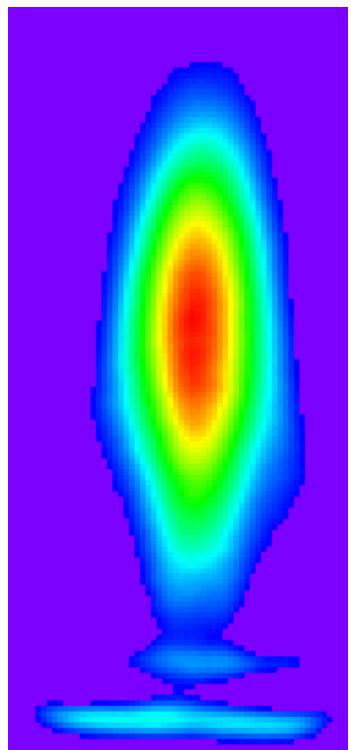


H=0.8 cm
Ar Boltzmann Plot

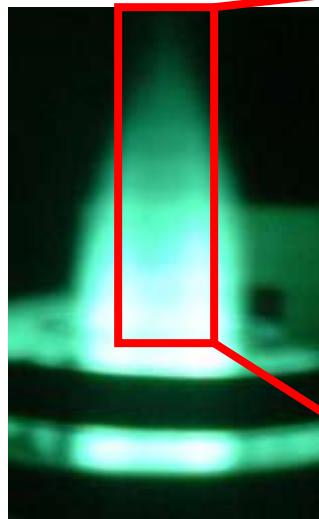




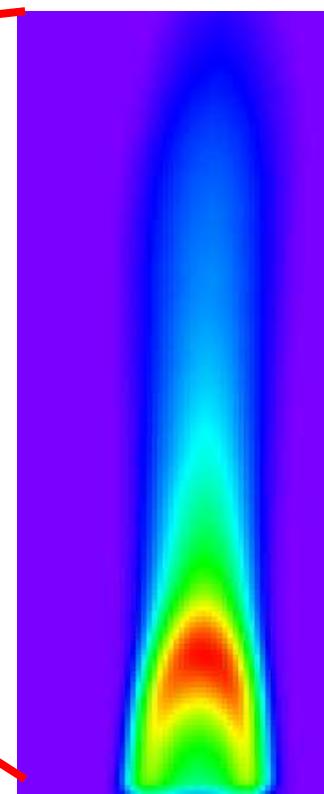
Boltzmann plot of Chromium triplets



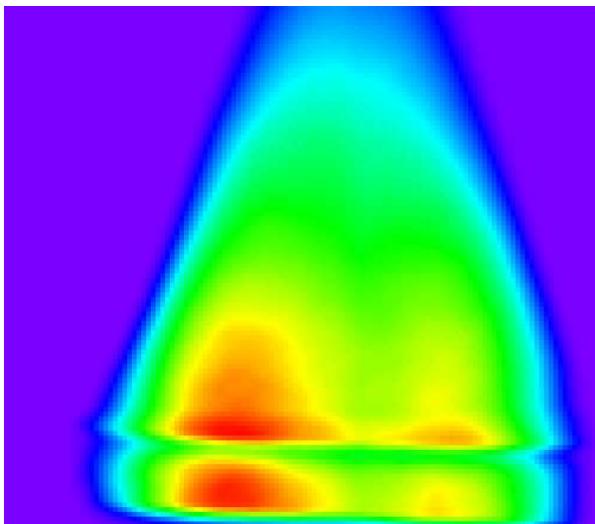
Fe ion



Ar atom



Cr atom



mm

18

12

0

-12

0

12

mm

20

10

0

-5

0

5

mm

20

10

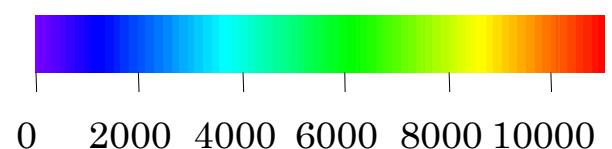
0

-7

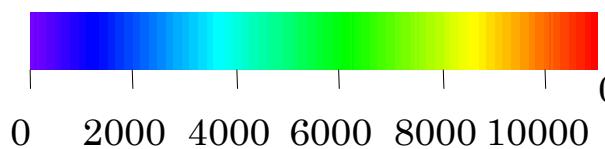
0

7

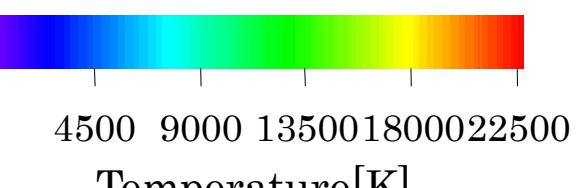
mm



Ar Excitation T

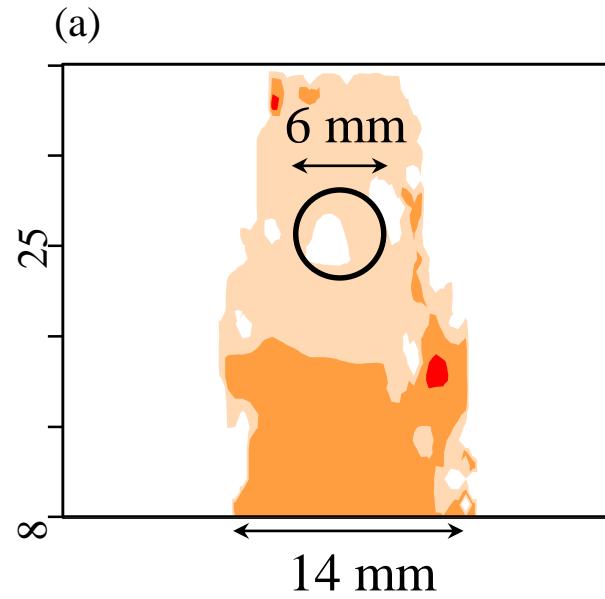


Cr atoms



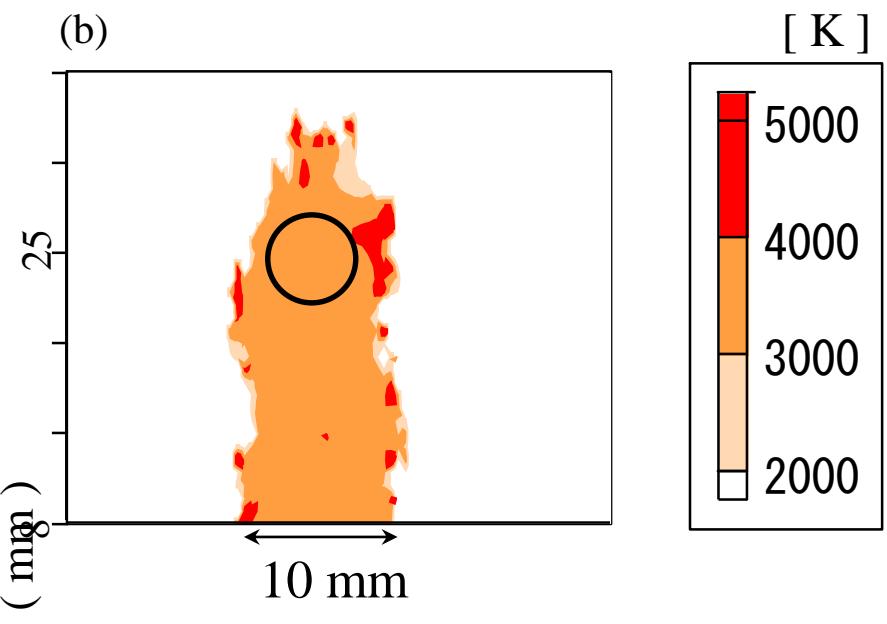
Fe ions

Distance from the top of coil (mm)



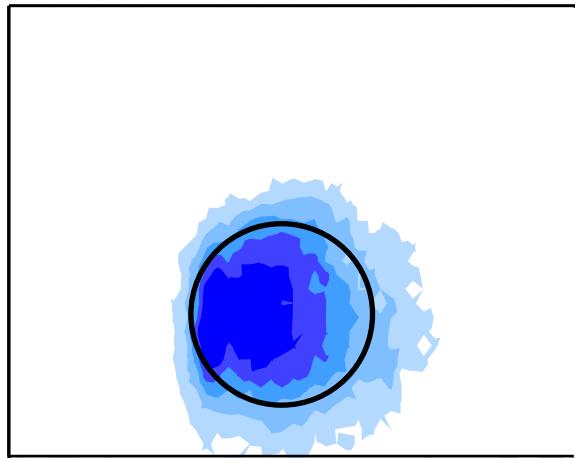
(a) inactive

Distance from the top of coil (mm)

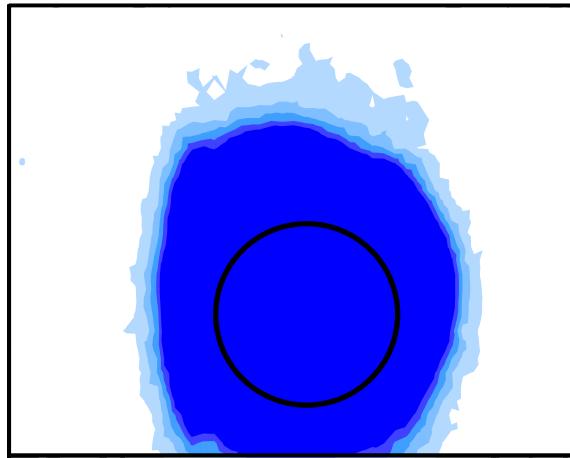


(b) oxidative

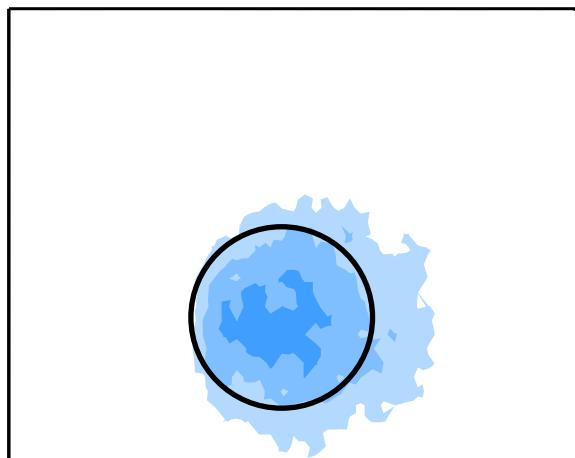
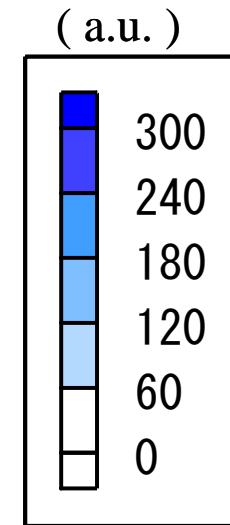
Spatial distribution of Fe excitation temperature with a graphite disk in plasmas under inactive and oxidative conditions.



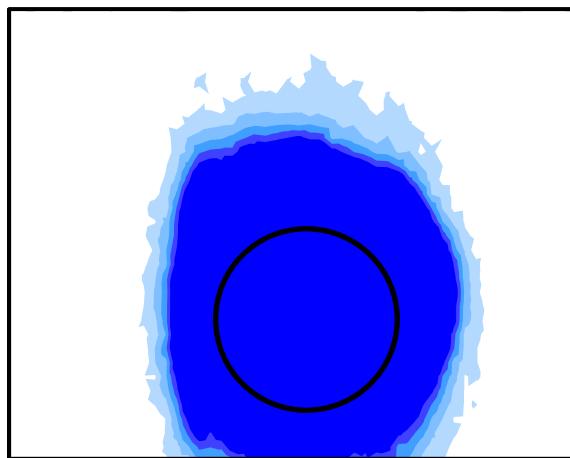
(a) under oxidizing conditions
after 20 s of exposure



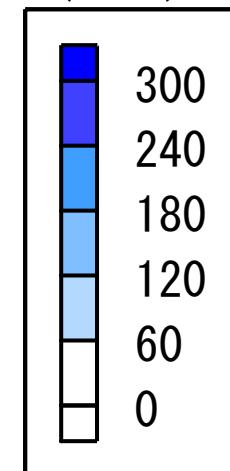
(b) under oxidizing conditions
after 200 s of exposure



(c) under inactive conditions
after 20 s of exposure



(d) under inactive conditions
after 200 s of exposure



Spatial distribution of spectral intensities of C emission around the C/C composite surface. 흑연 디스크의 주위의 탄소 원자 발광의

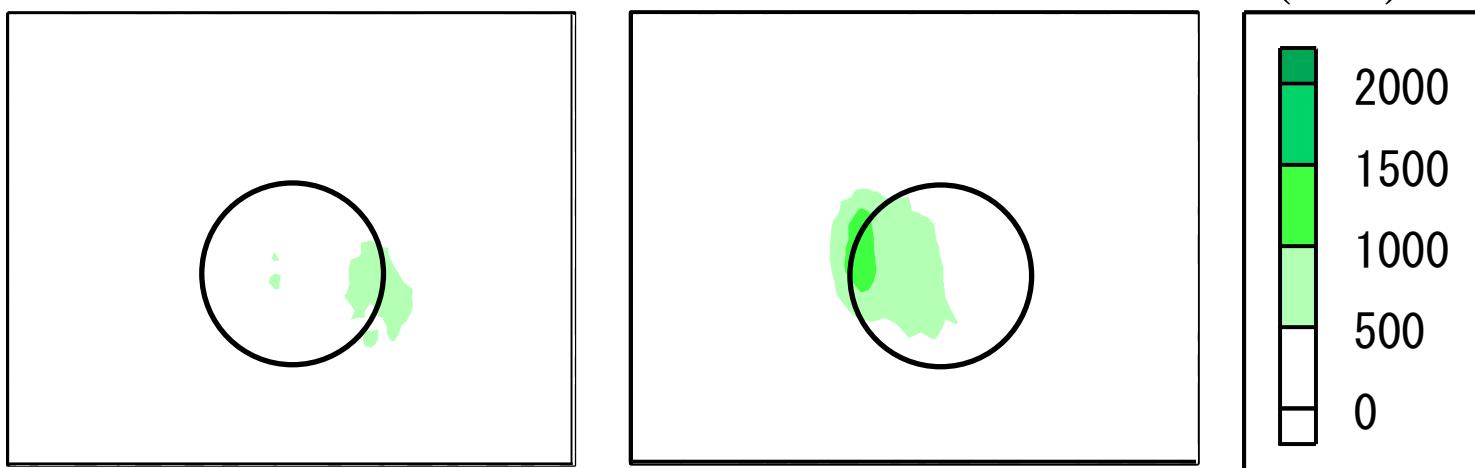
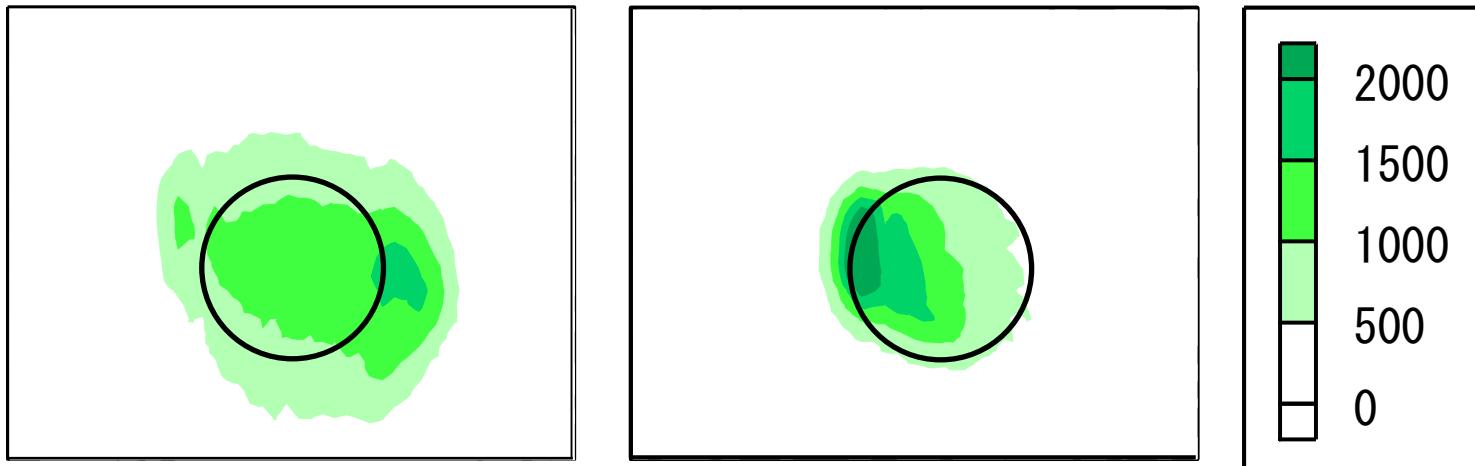
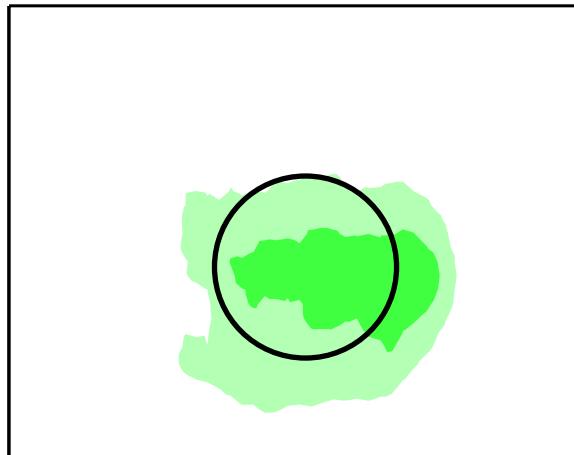
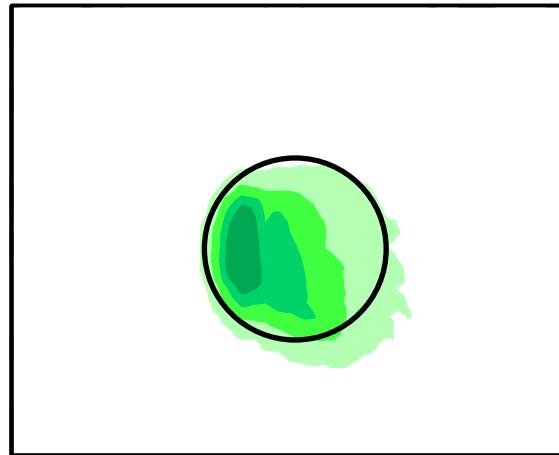


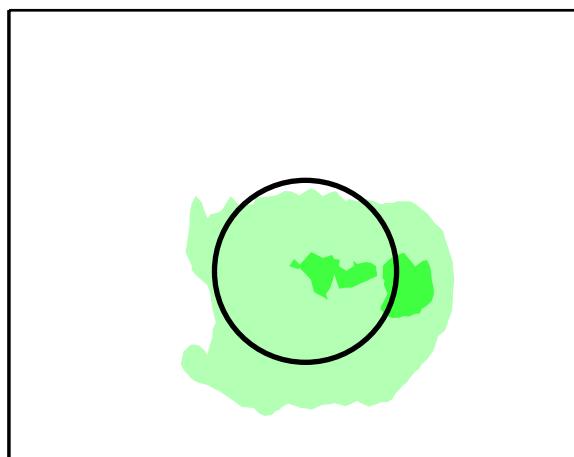
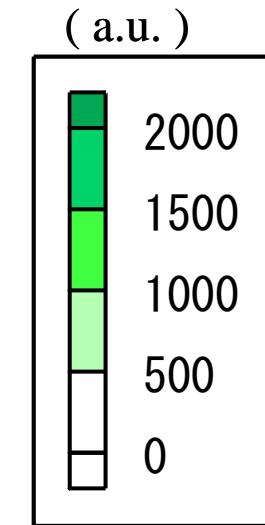
Fig. 5. Spatial distribution of spectral intensities of Si emission around the C/C composite surface with the double layer coating surface.



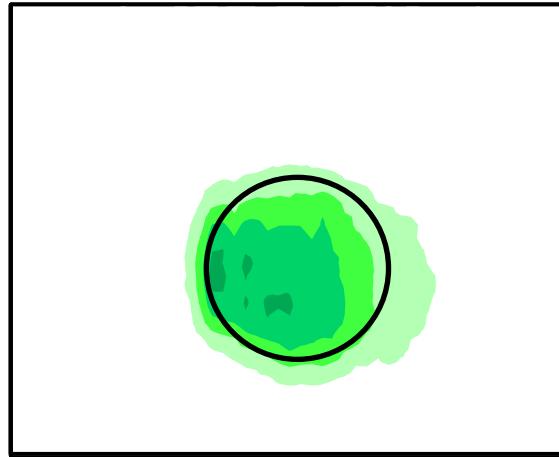
(a) Under oxidizing conditions
after 20 s of exposure



(b) under oxidizing conditions
after 200 s of exposure



(c) under inactive conditions
after 20 s of exposure



(d) under inactive conditions
after 200 s of exposure

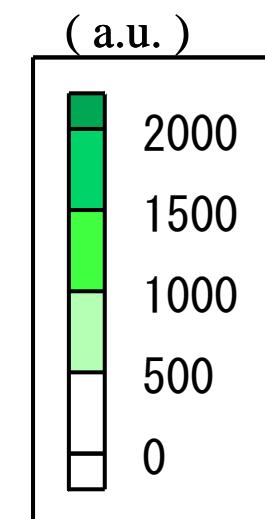


Fig. 6. Spatial distribution of spectral intensities of Si emission around the SiC disk surface.

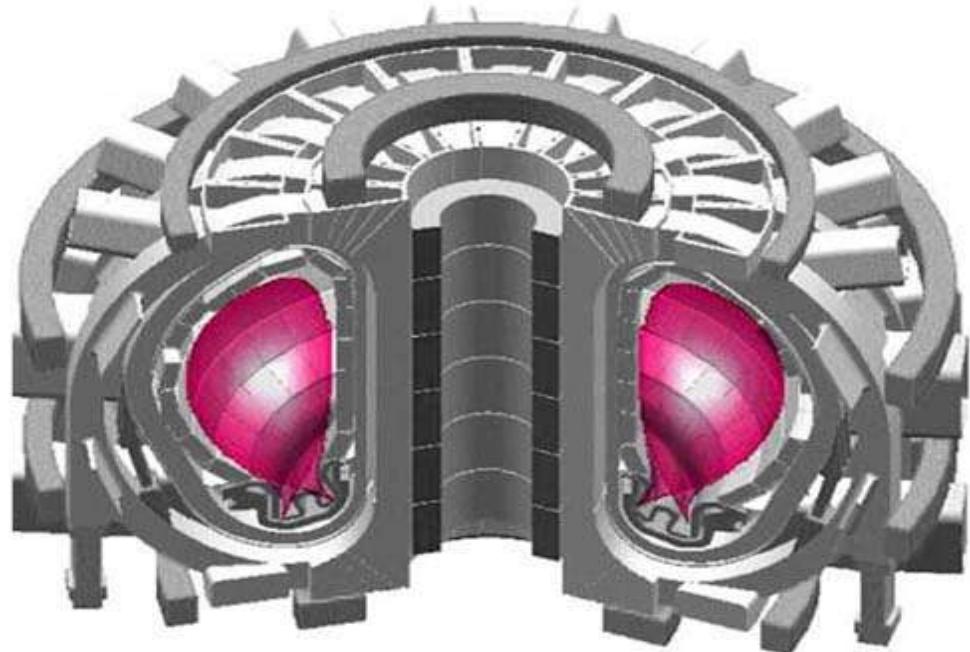
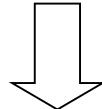
Nuclear Fusion Plasmas

$D + D \text{ or } D + T \rightarrow He + \text{Energy}$
No CO_2 emission

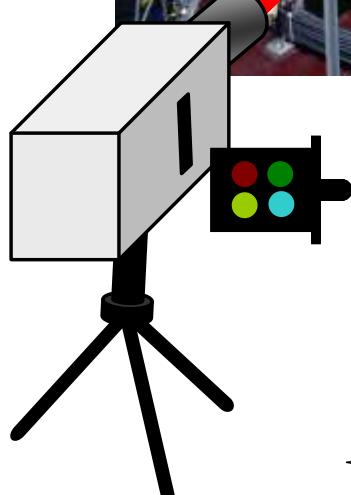
Issues

1. Ignition

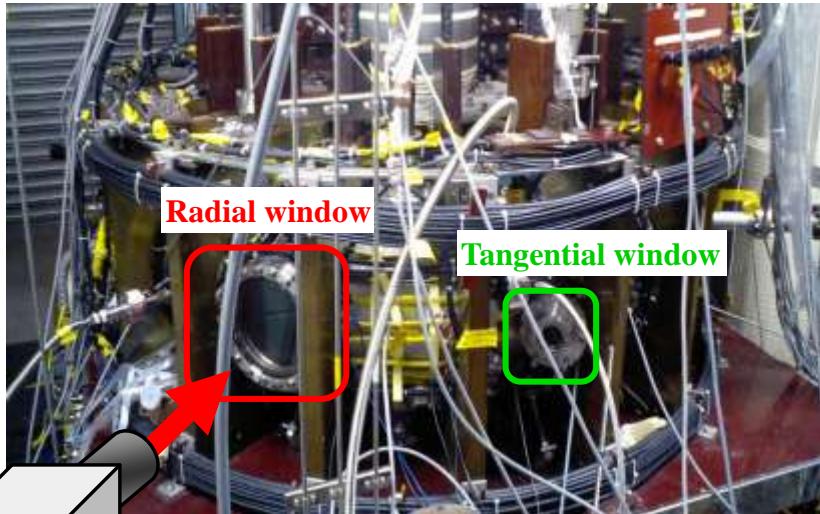
2. Damage on Reactor
Carbon Linings:
Chemical Sputtering



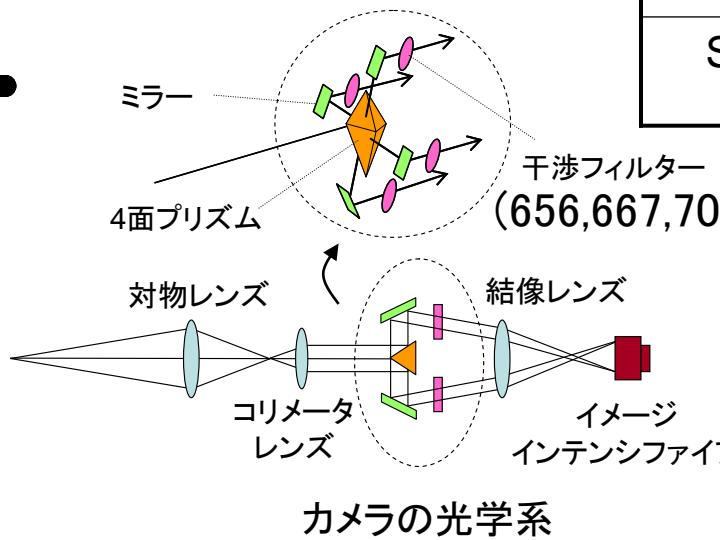
HYBTOK-II



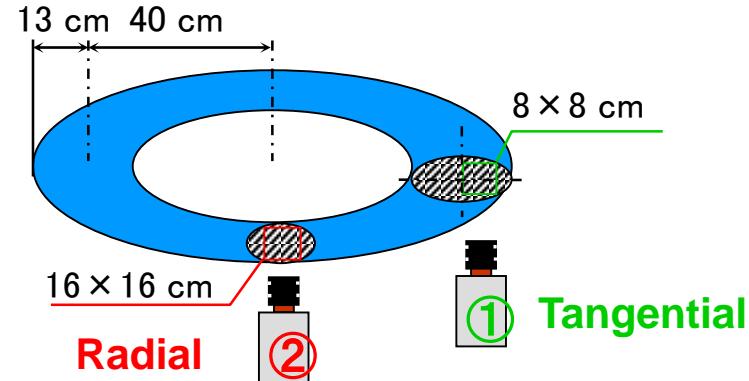
High speed 4-Ch
Video camera



Tangential window



カメラの光学系



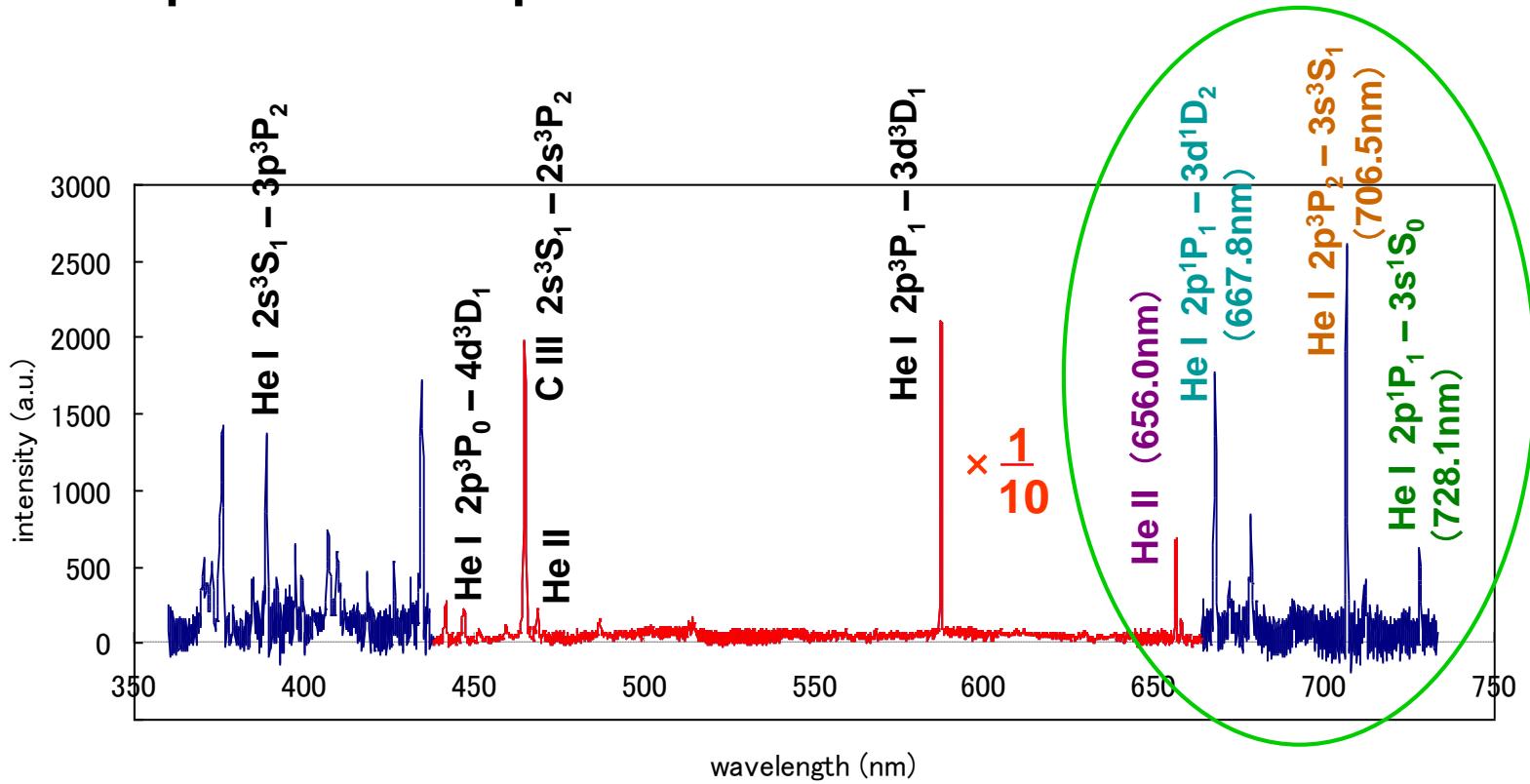
HYBTOK-II physical properties

L. d.	40 cm	Plasma gas	He
S.d	13 cm	Discharge duration	~20 ms

Video Camera Conditions

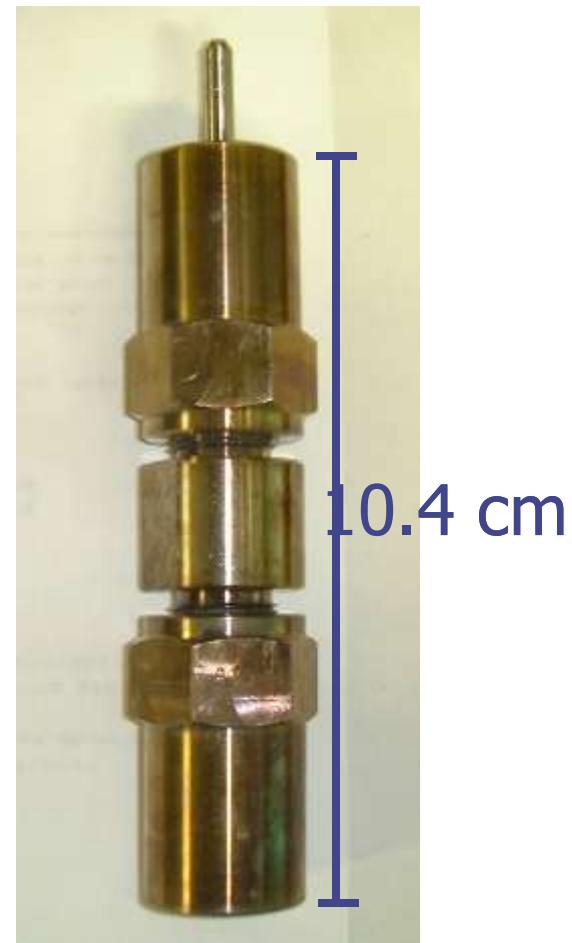
frame rate	2000,6000 fps
Intensifier gain	1.2 ~ 4.6
Focus length	50 mm
F	1.2

Spectrum for a plasma for helium atoms and ions



Hydrothermal Process

- Biomass sample : 0.1 g
- Distilled H₂O / D₂O : 3 ml
- Additives :
 - Sodium carbonate (Na₂CO₃)
 - Nickel catalyst (Ni / SiO₂)
- Reaction Temp. : 400°C
- Pressure : ca. 25 MPa



Microtube reactor
(10.5 ml)

Hydrothermal gasification of biowaste

- Cellulose
(Model biomass sample)



◆ Real biomass

Wasted wood



C: 46.1 wt% H: 6.1 wt%
N: 1.5wt% S: 0.7 wt%

"Okara"



C:46.2 wt% H: 6.7 wt%
N: 6.1 wt% S: 0.9 wt%

Fertilizer



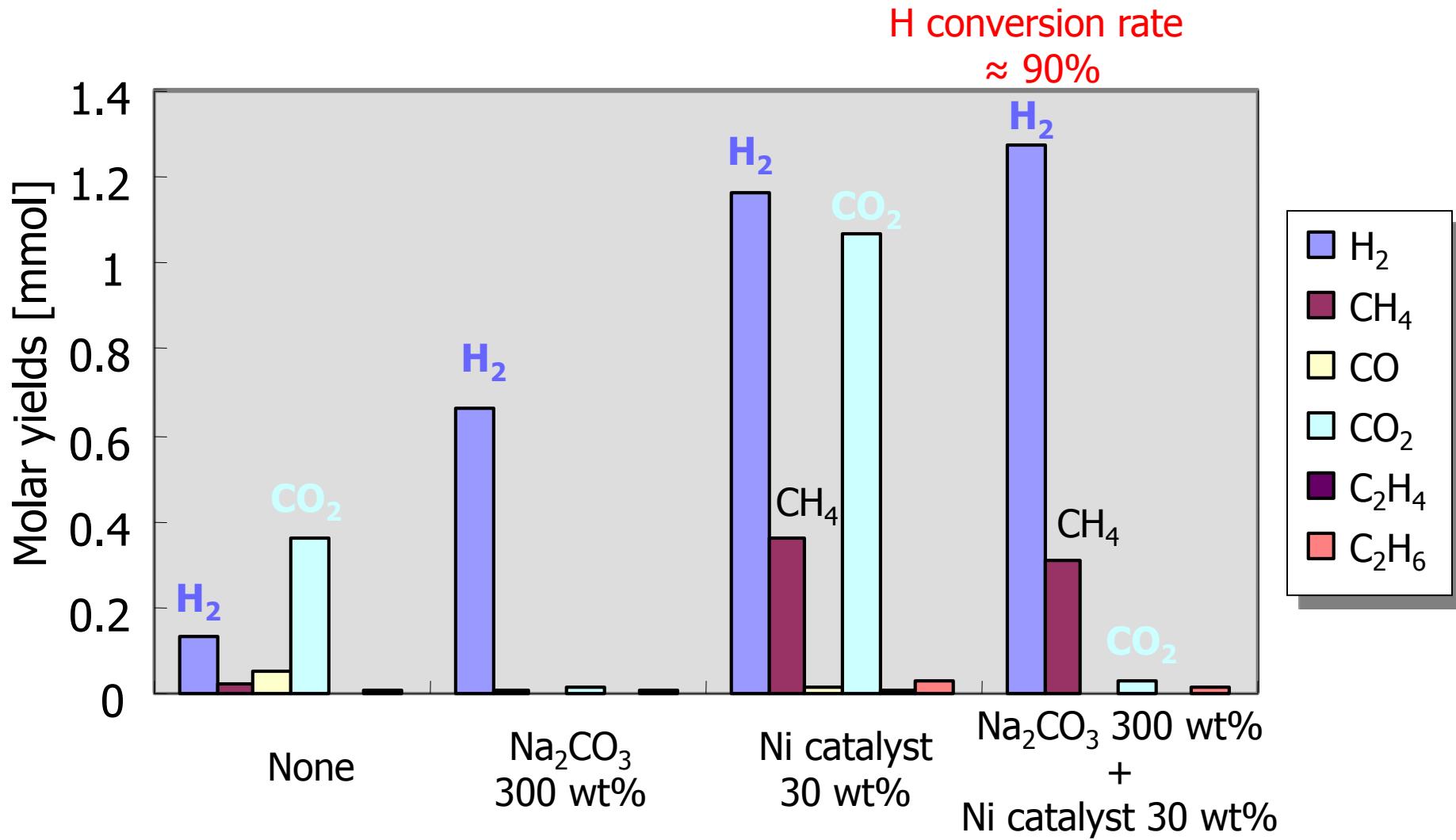
C: 34.8 wt% H: 5.3 wt%
N: 7.6 wt% S: 1.3 wt%

Peat

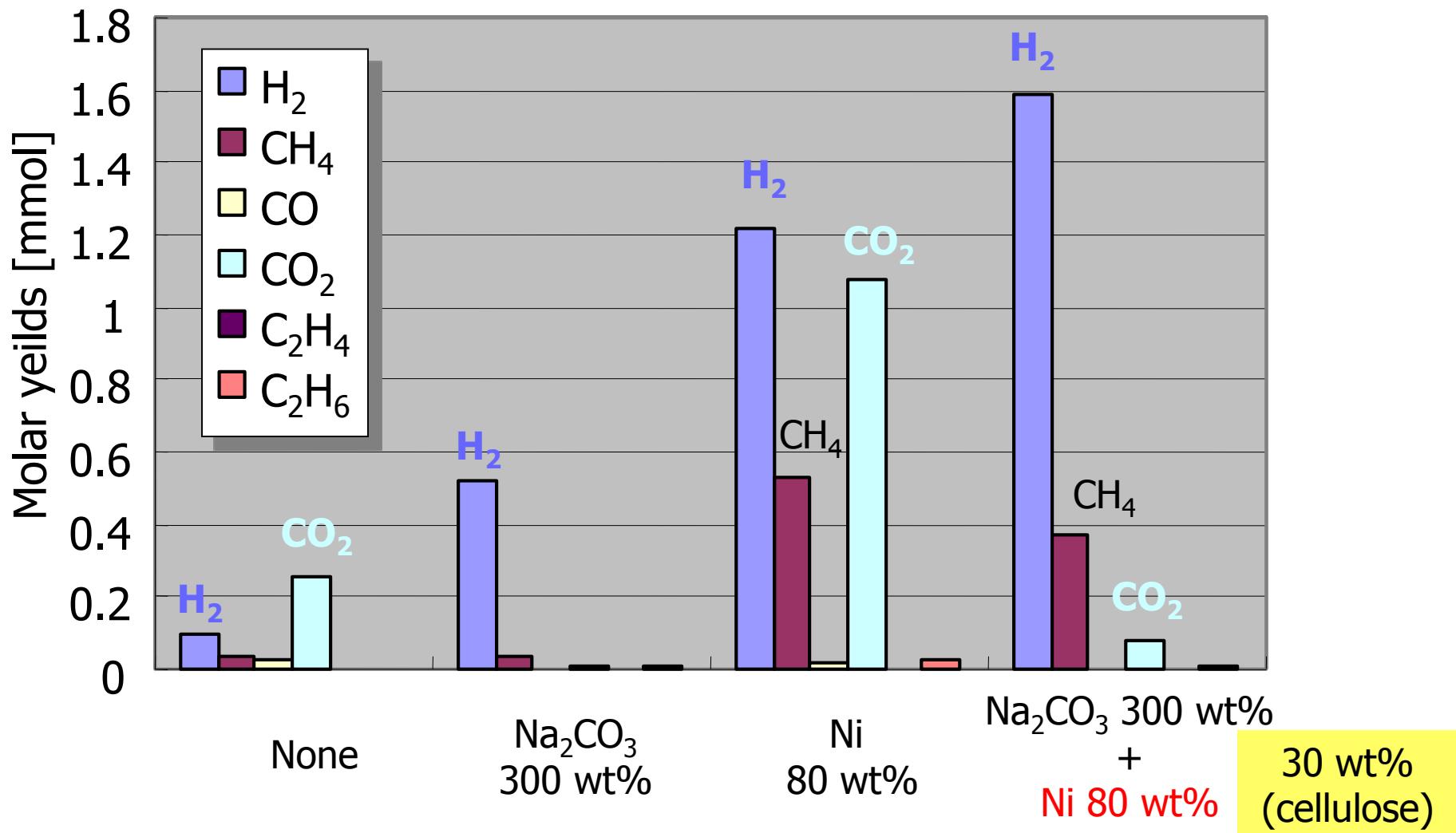


C: 46 wt% H: 5 wt%
N: 1 wt% O: 38 wt%

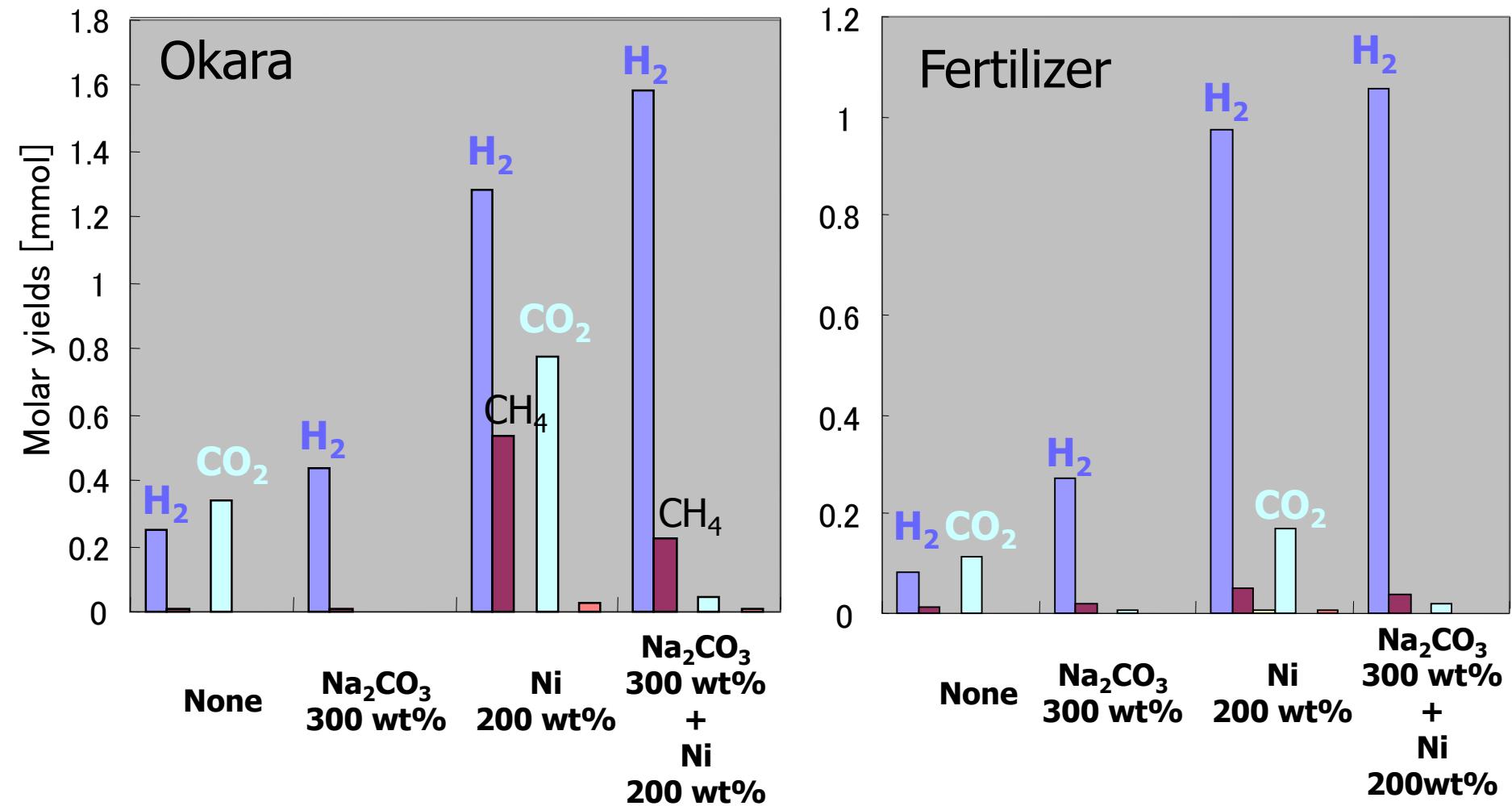
Effect of Na_2CO_3 and Ni Catalyst on Hydrothermal Reaction of Cellulose

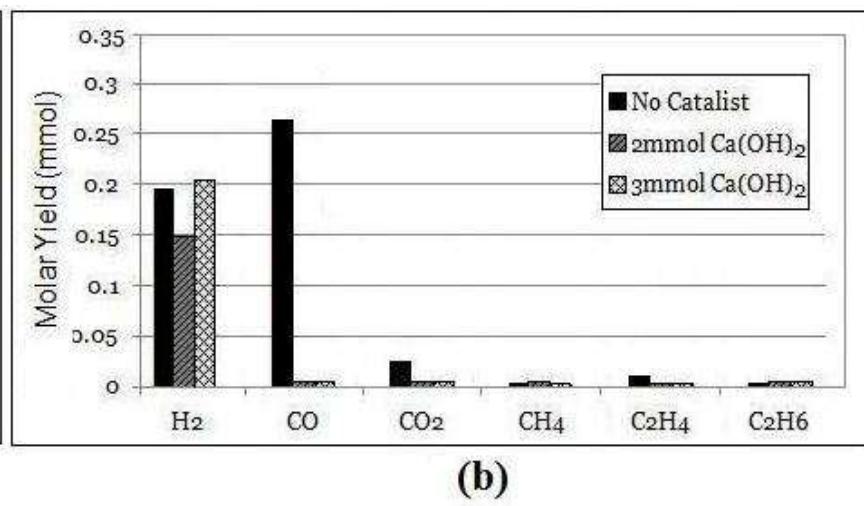
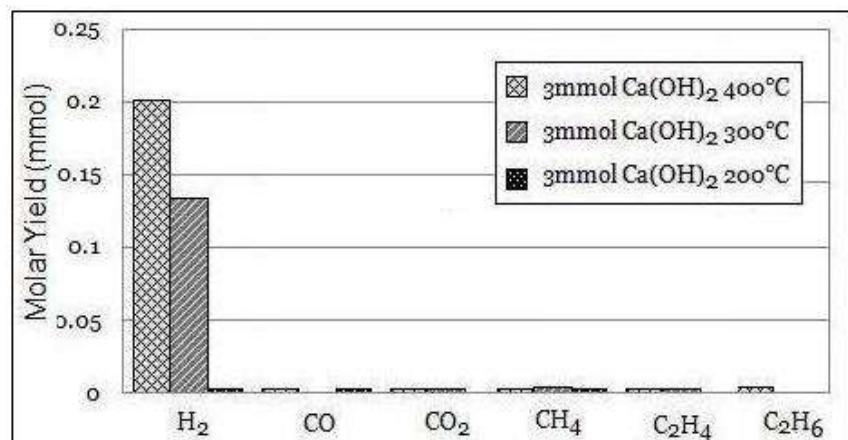


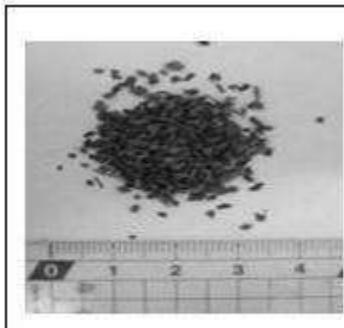
Effect of Additives on Hydrothermal Reaction of Wasted Wood



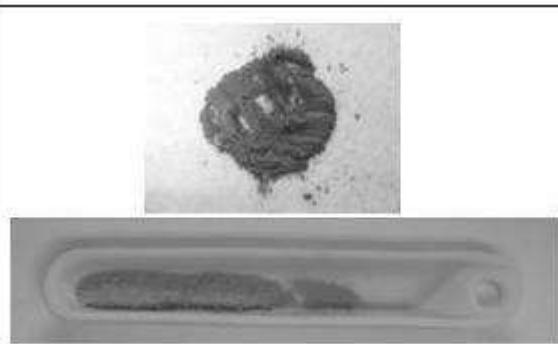
Effect of Additives on hydrothermal Reaction of Okara and Organic Fertilizer



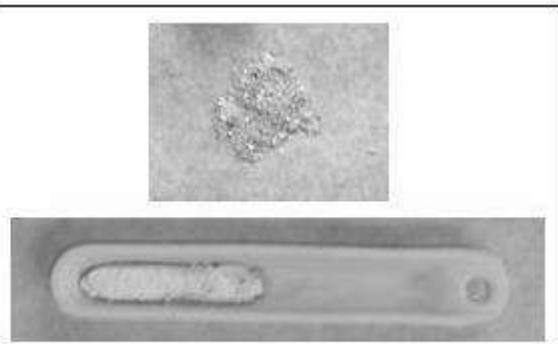




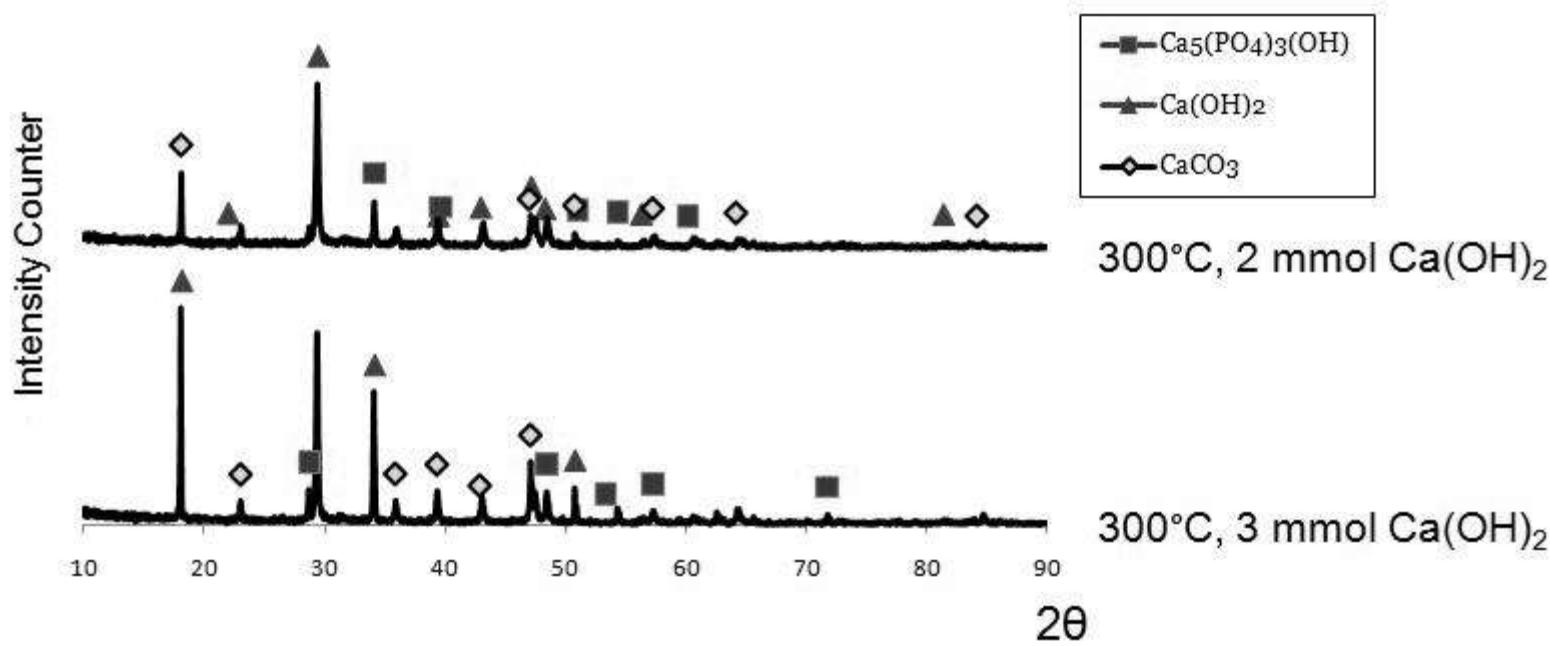
(a)

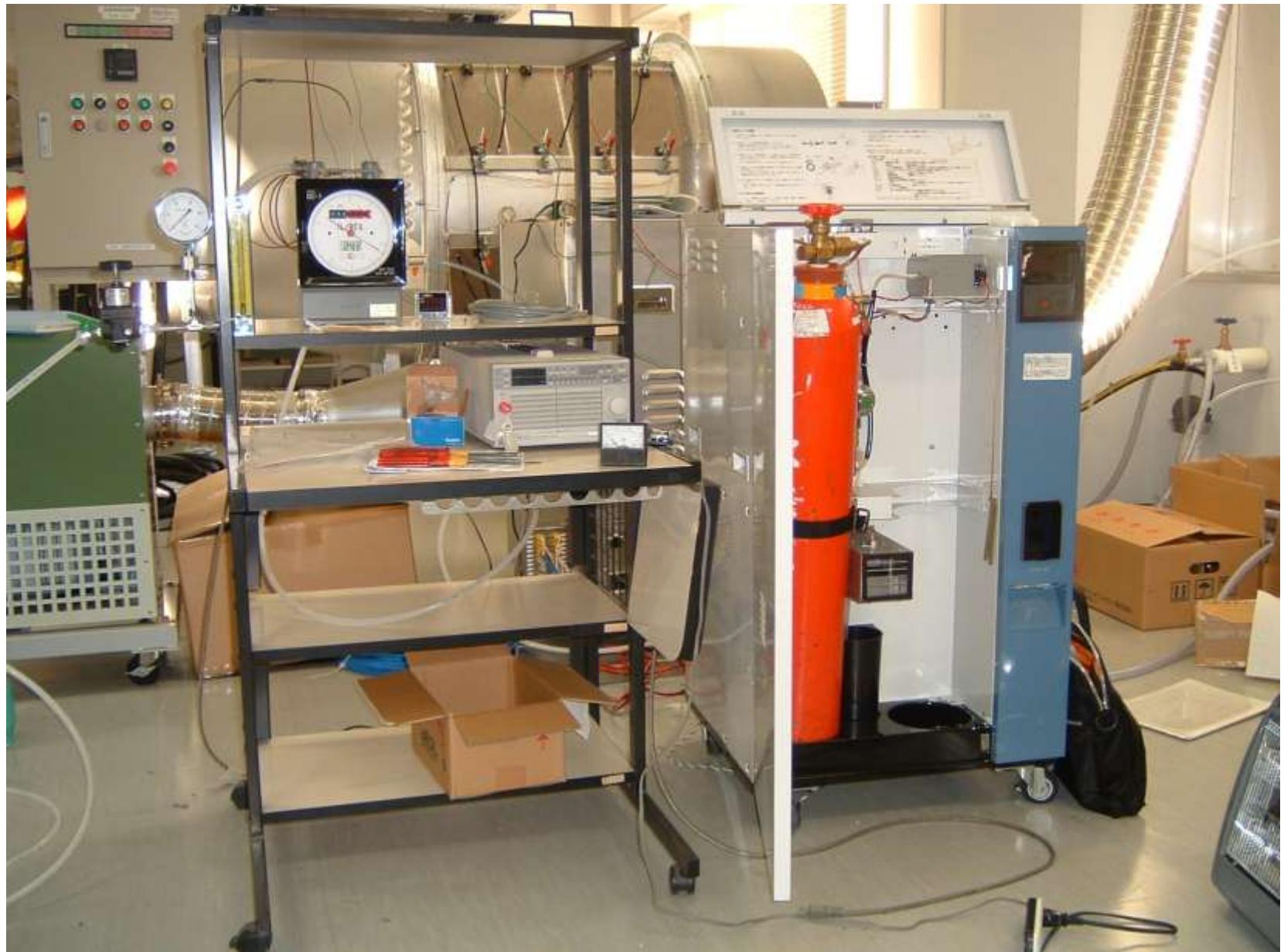


(b)

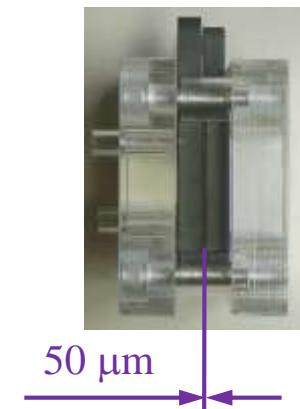
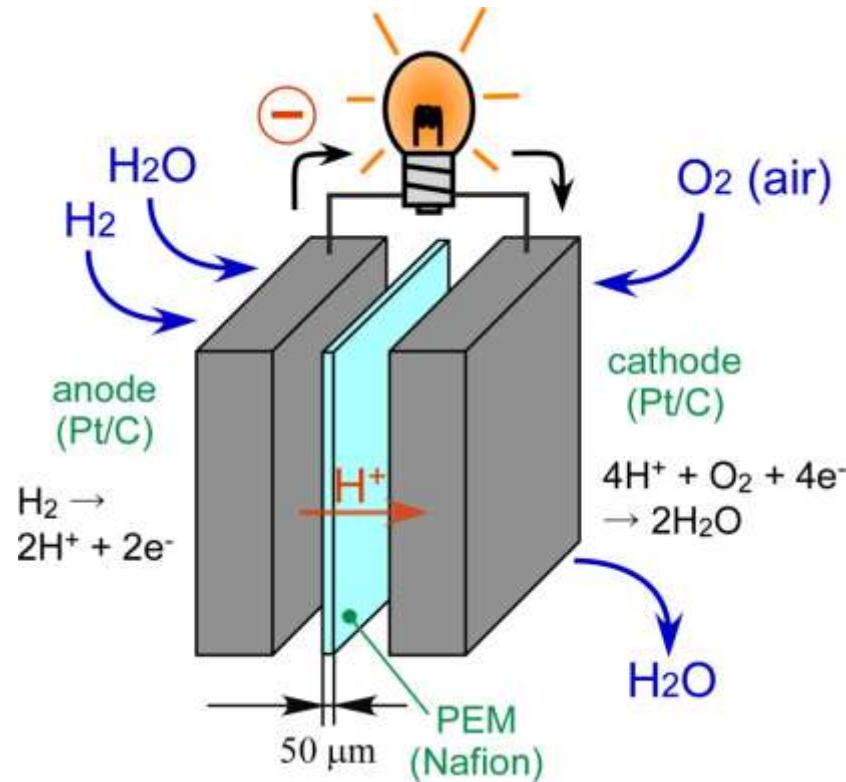


(c)



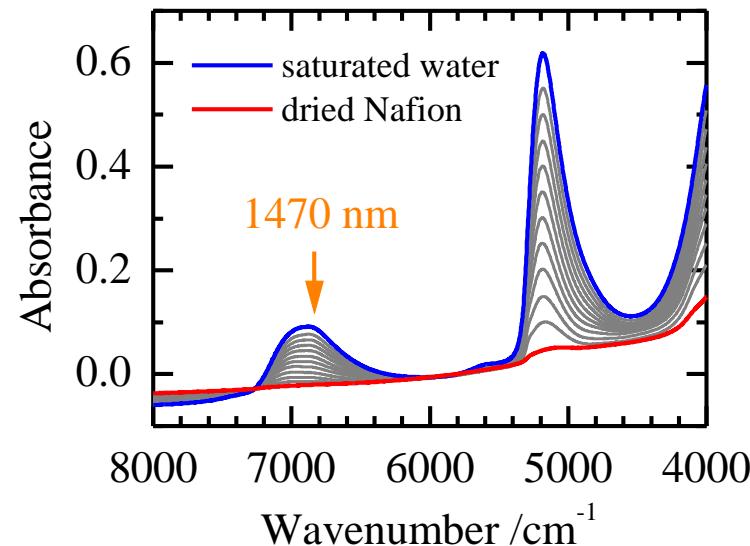
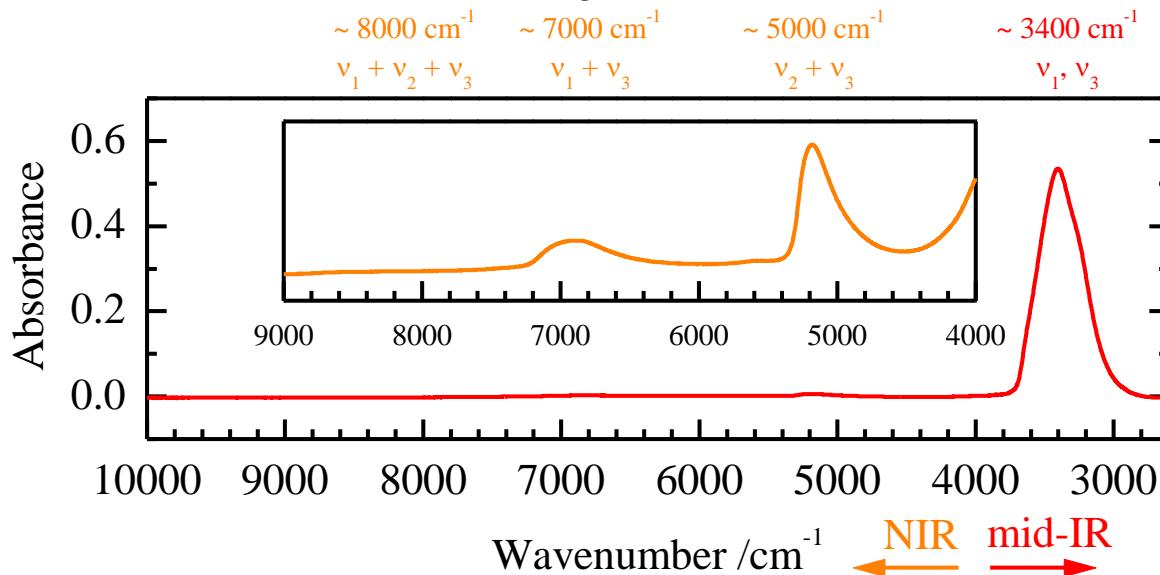


In situ monitoring of water in a PEM

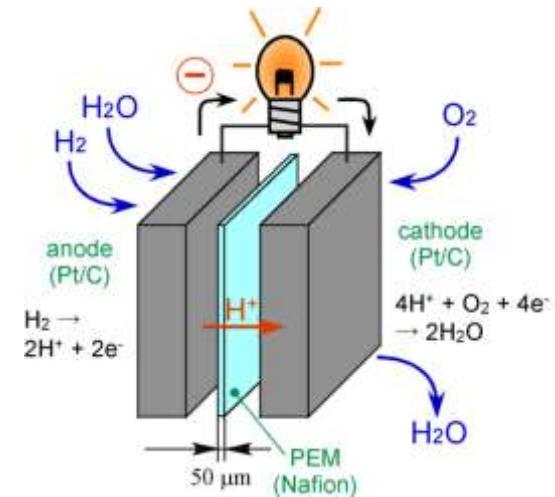
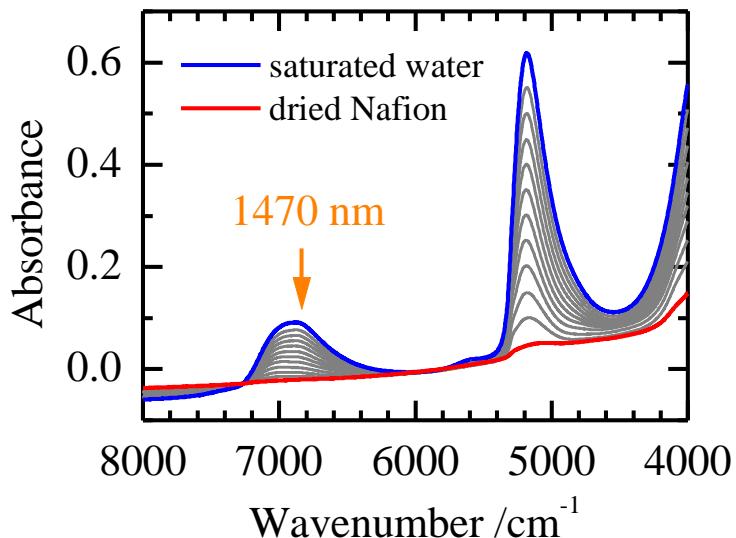
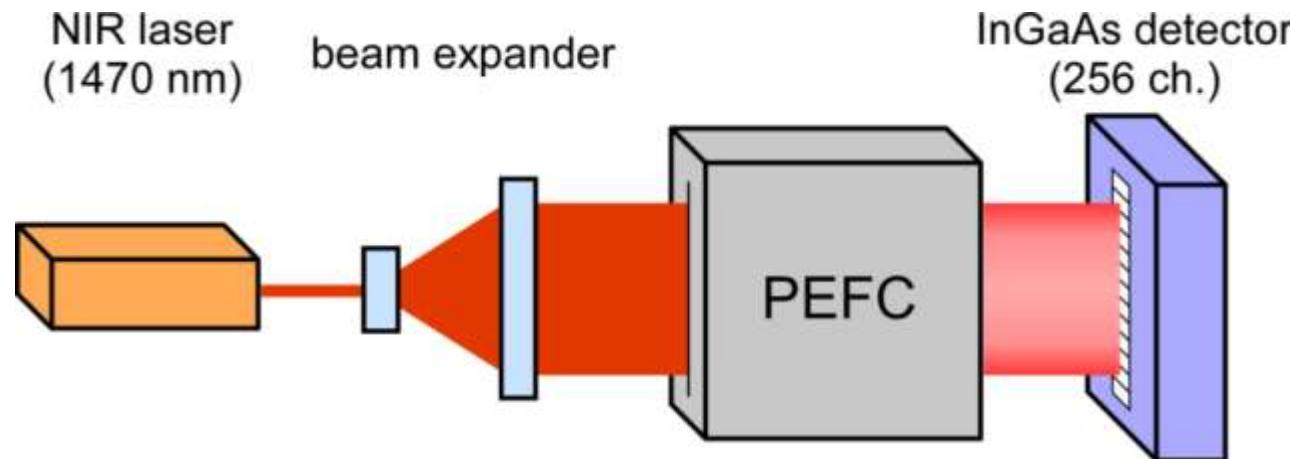


In situ monitoring of water in a proton exchange membrane (PEM) is important but difficult because the then membrane is sandwiched between two opaque electrodes. We have developed **near-infrared (NIR) laser spectroscopy** for the detection.

【Why NIR?】

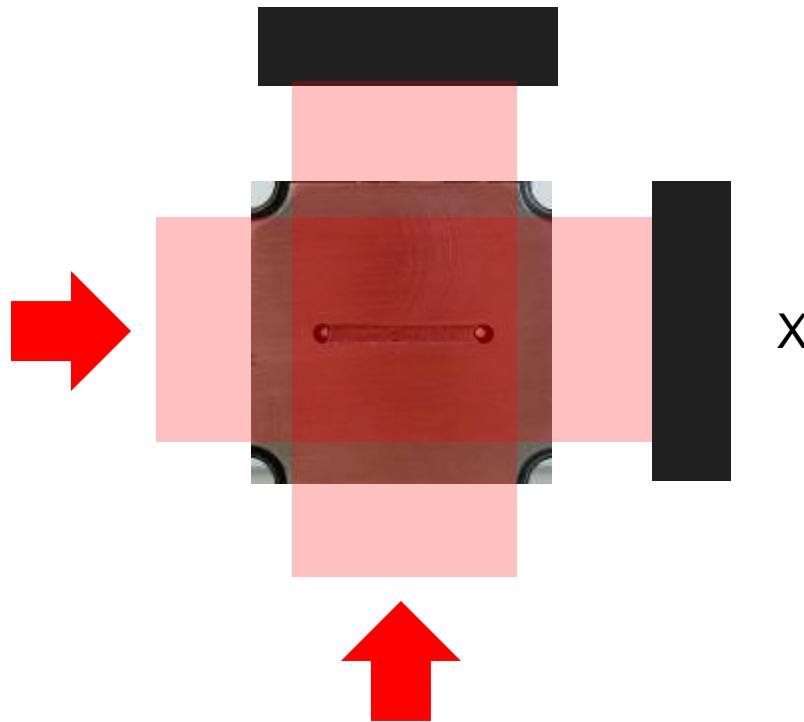


(NIR Laser Detection of Water)



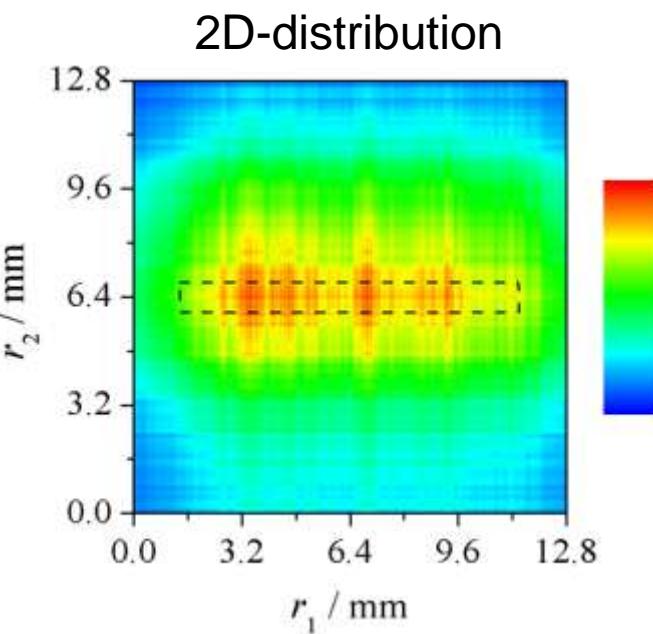
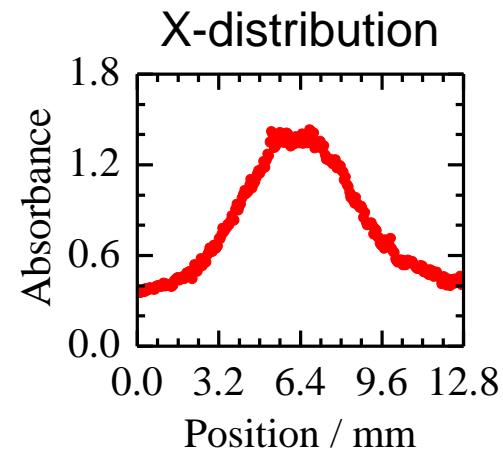
【2D Water Distribution】

Y One-way linear gas flow channel



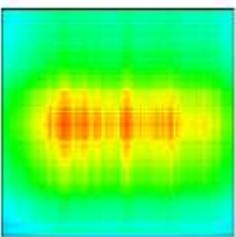
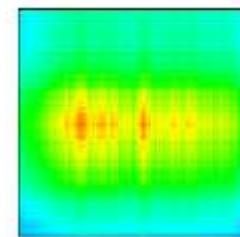
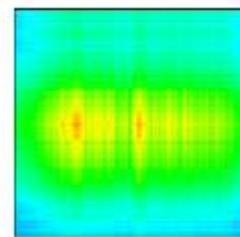
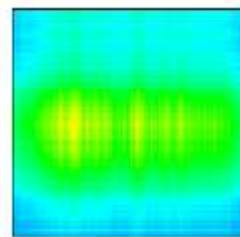
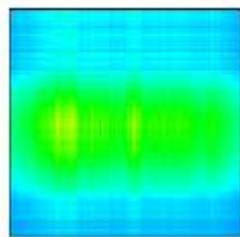
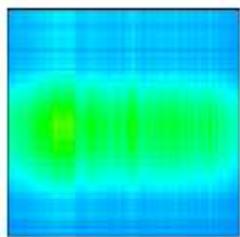
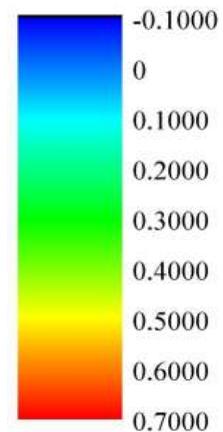
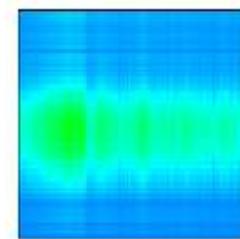
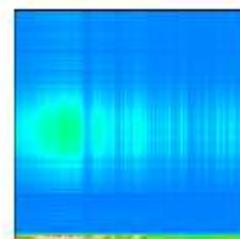
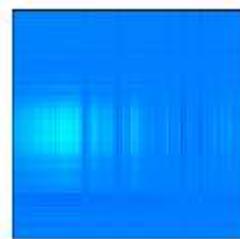
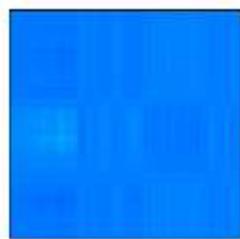
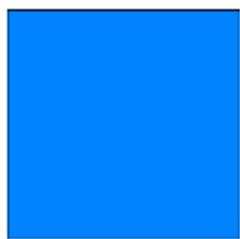
(X-distribution)

$$\times \text{ (Y-distribution)} = \left[\begin{array}{c} \text{2D-distribution} \end{array} \right]$$



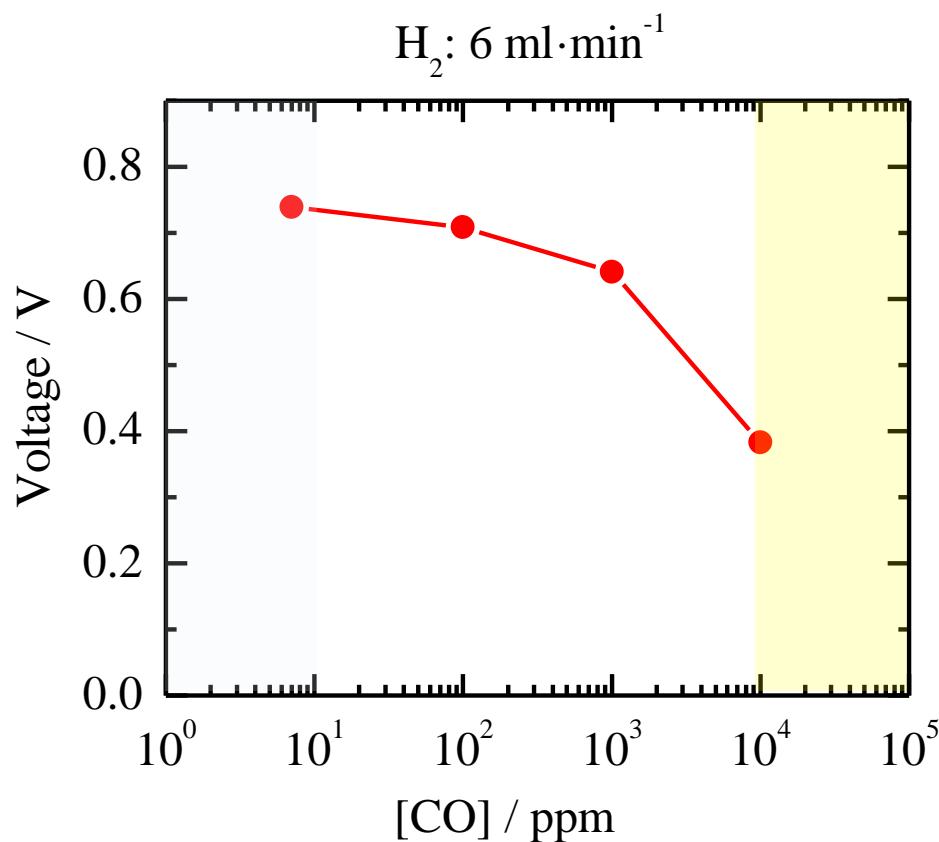
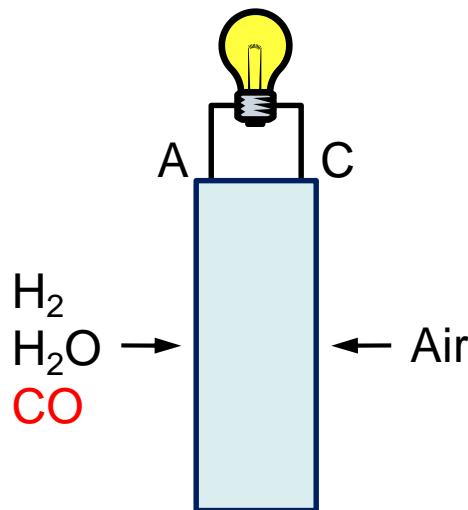
【2D imaging by NIR laser】

1 frame / min.



H_2 , water

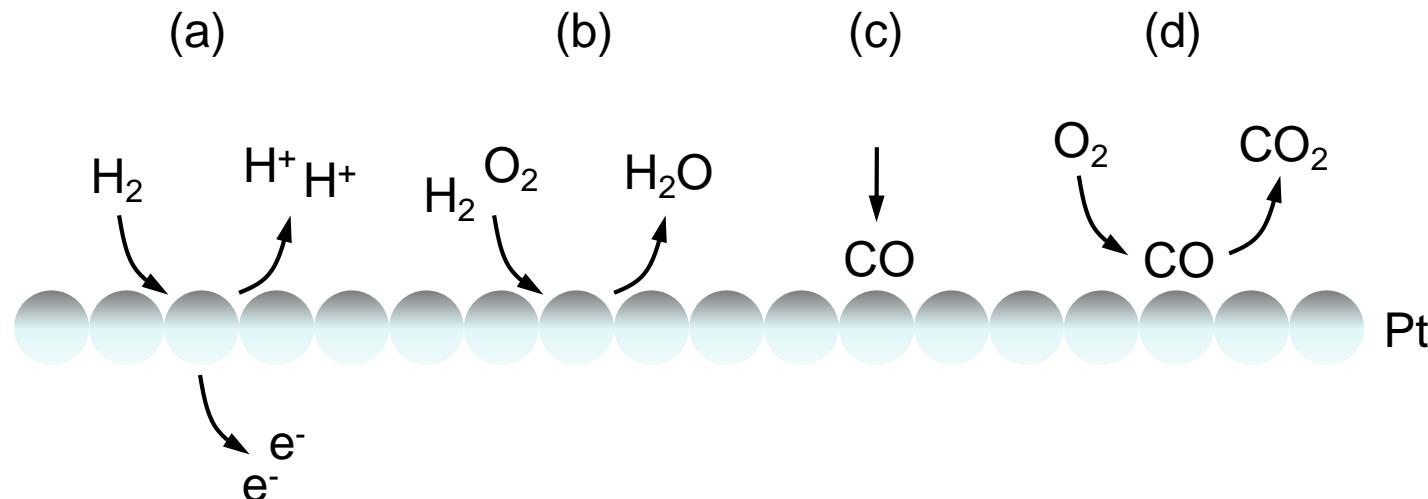
【CO poisoning onto a Pt catalyst】



A hydrogen gas produced from hydrocarbons by steam reforming generally contains residual carbon monoxide ($10^4 \sim 10^5$ ppm). PEFC requests less than 10^1 ppm level of the residual CO.

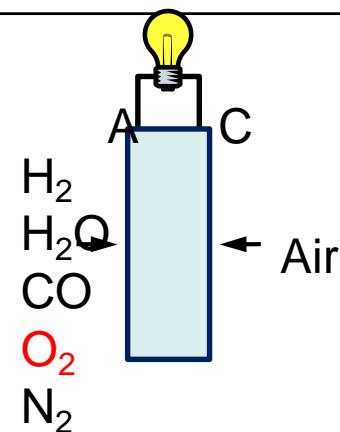
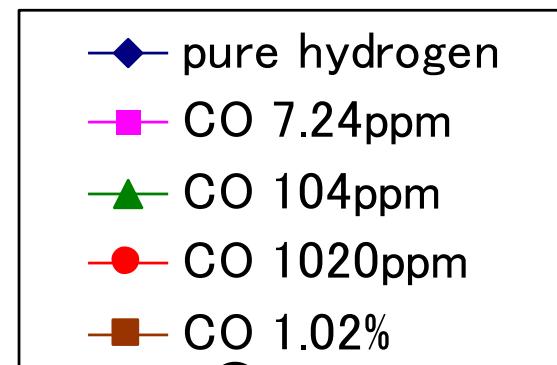
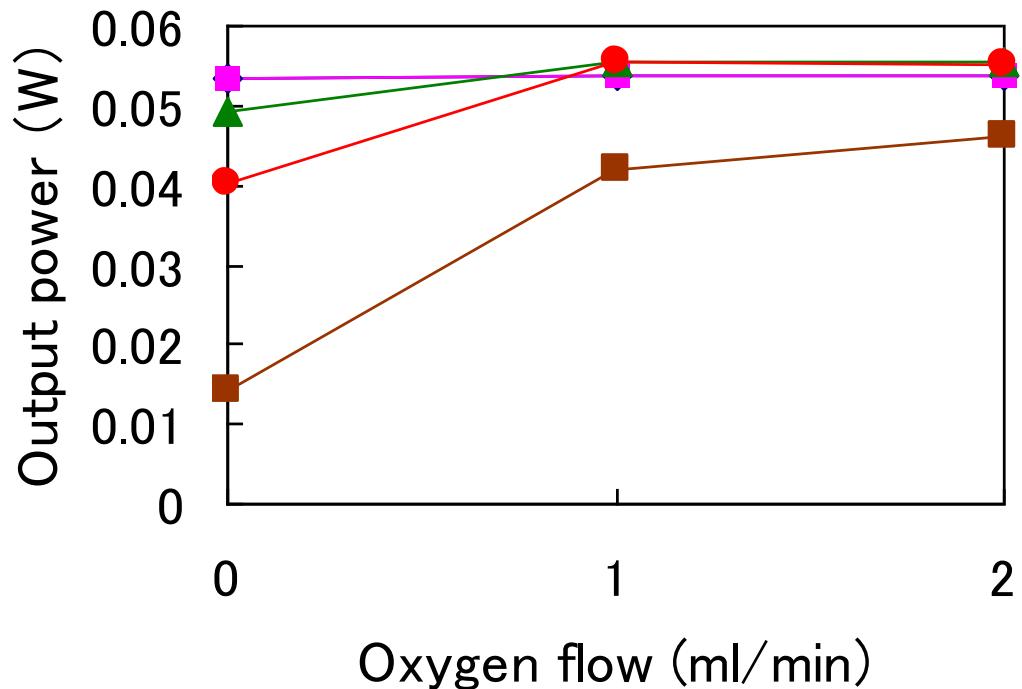
【Catalysis at the Pt surface】

- (a) Production of H^+
- (b) Oxidation of H_2
- (c) CO poisoning
- (d) Oxidation of the adsorbed CO



Result

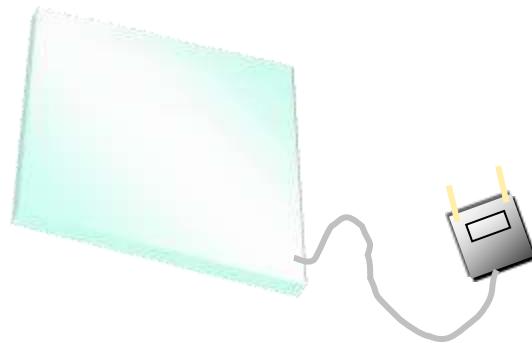
$\text{H}_2 + \text{CO}$ ca.6mL/min
 $\text{N}_2 + \text{O}_2$ ca.3mL/min



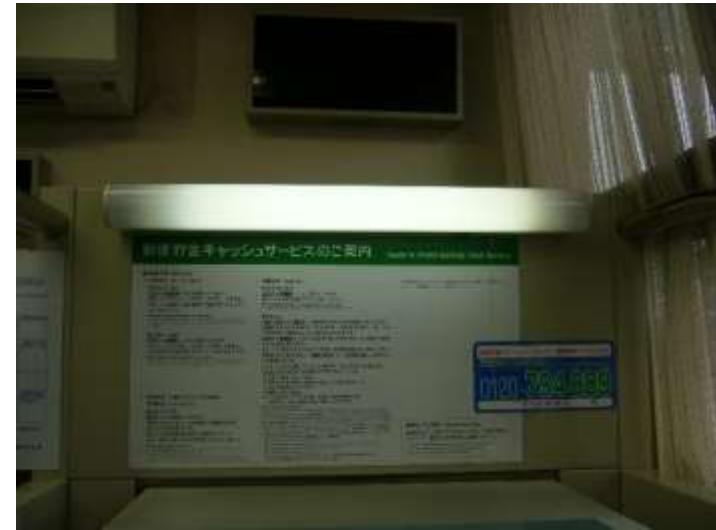
The deactivation by high concn. CO can successfully be suppressed.



“Thin LED Panels for Soft and Uniform Illumination”



Conventional Fluorescent Lamps



開発の目的

Advantages of LEDs

Long life 70000hrs:7-10 times FL

No Hg waste (ca.3 tons/year in Japan)

Safety: Low voltage

Too bright point emission

Advantages of LED panels developed

Long life time: continuous operation for up to 70,000 hrs

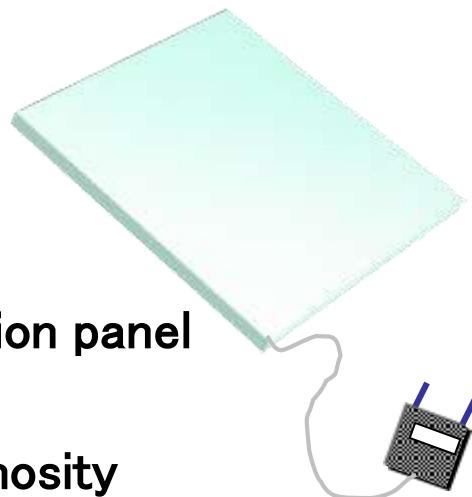
Light : ca.1kg in letter size

Thin: 2–5 mm

Uniformity: uniform luminescence for diffusion panel

Power Control: Smooth adjustment of luminosity

Safety: Low unit driving voltage up to 15 V



Evaluations

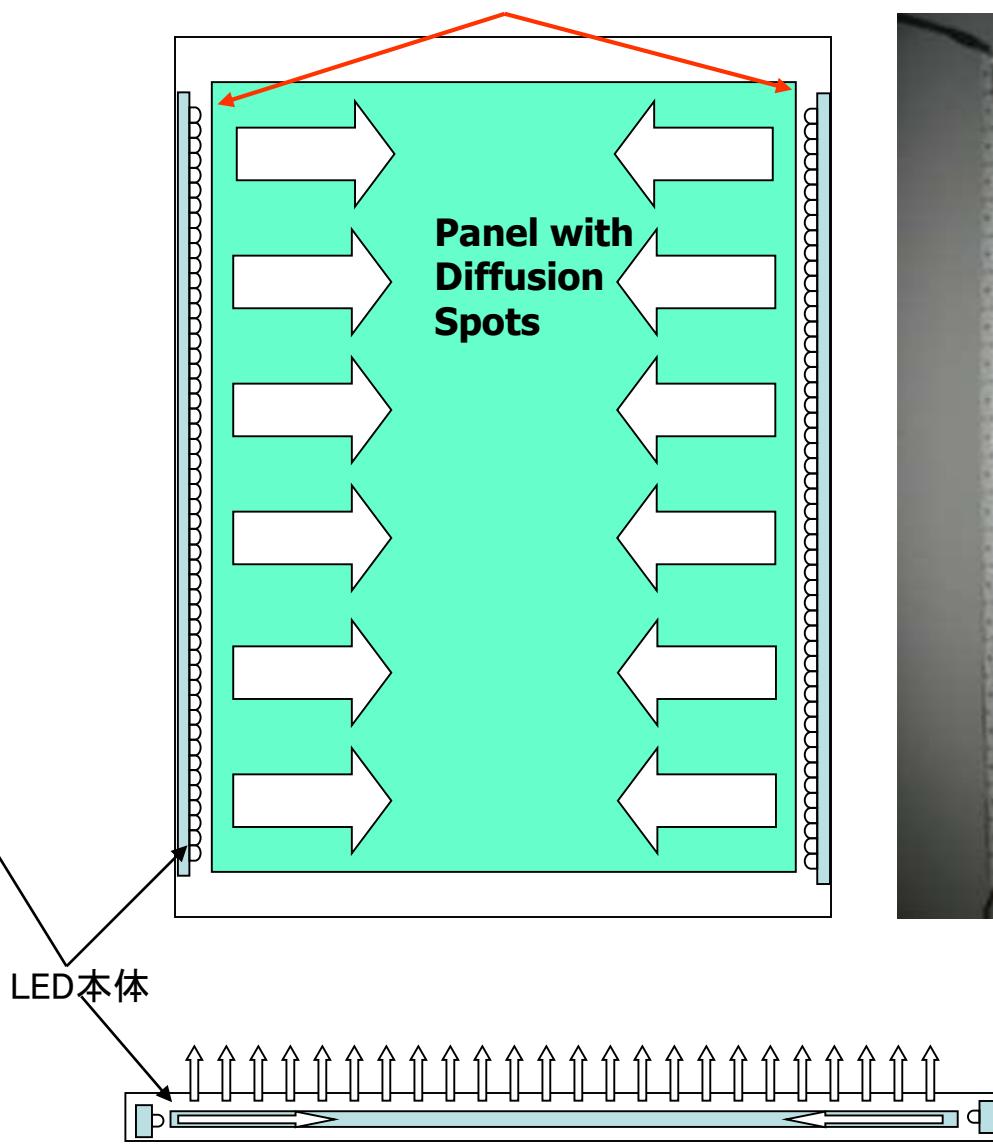
- 1. White LED panels: luminosity and power consumption**
- 2. Human effect of pulse operation**
- 3. Eye fatigue evaluation**
- 4. Color temperature control**

Thin LED panel

LED array

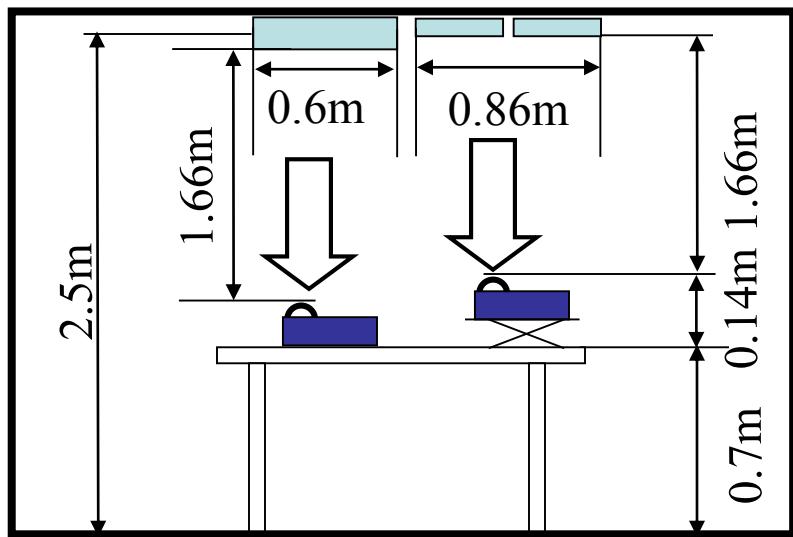


Double sides



Test layout

20WtypeFL CW-LED
10Wx2



Power consumption



LEDx2

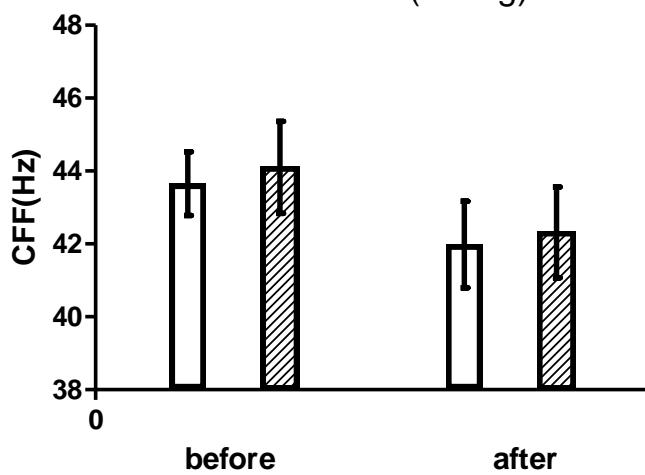
102.2Lx(100V/25W)

FL

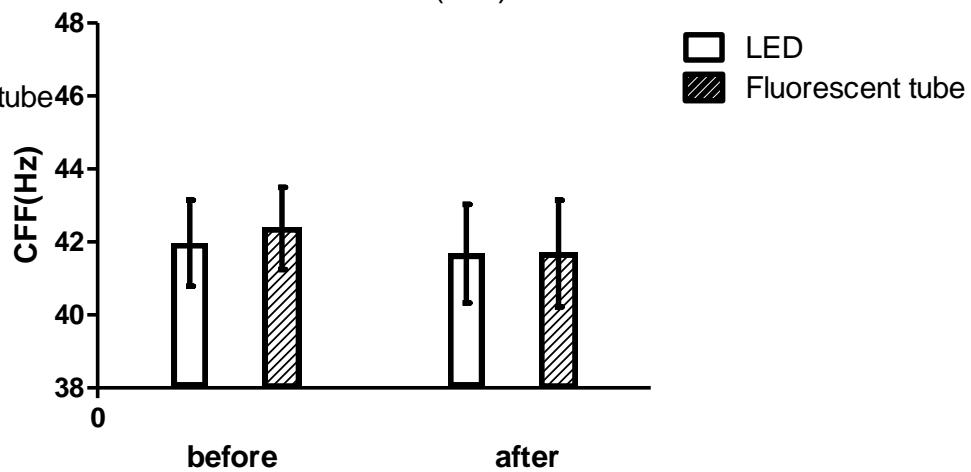
99.1Lx(100V/25W)



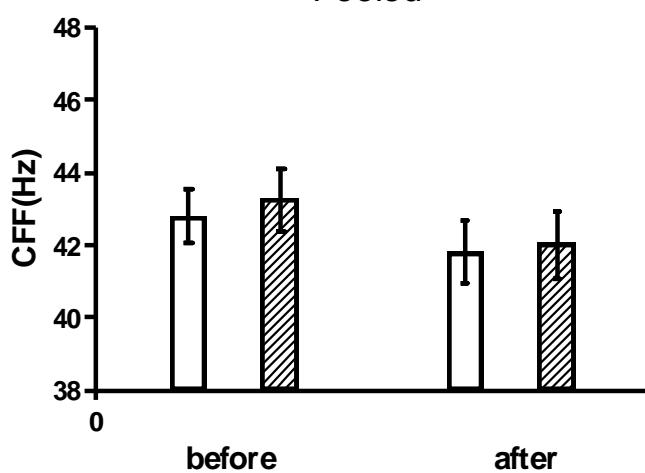
Man+Woman(Young)



Man+Woman(Old)

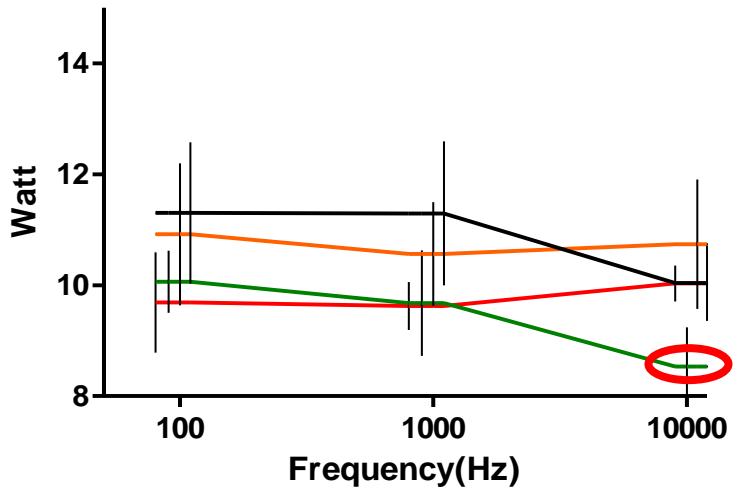


Pooled

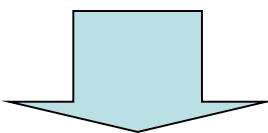
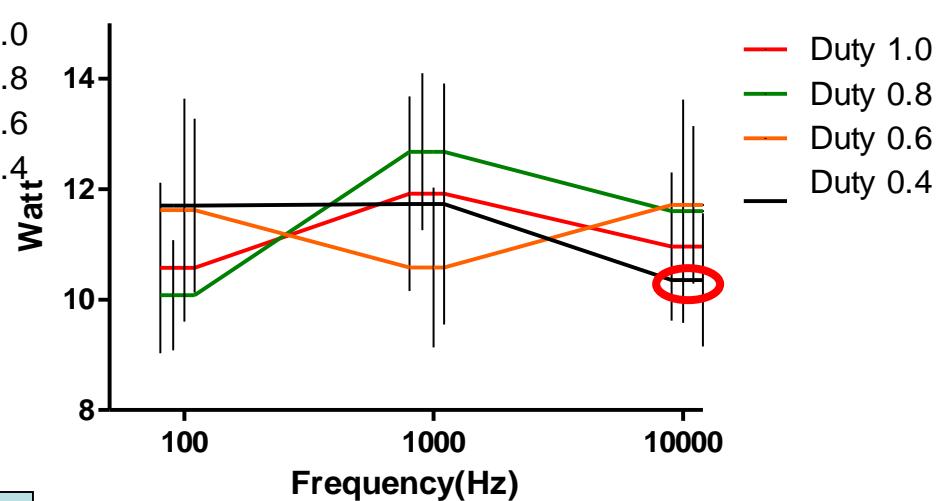


No difference: The LED panel can be used for an alternative as FLs.

Young(Man+Woman)



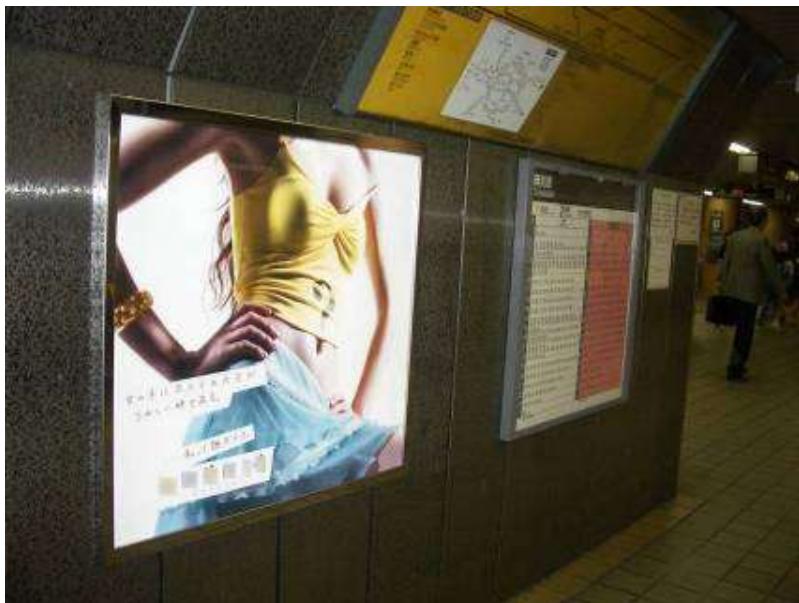
Old(Man+Woman)



	Duty ratio	Power reduction
Young	0.8	15%
Aged	0.4	5.6%

Commercial application 1

Nagoya City Subway Station



Commercial application 2

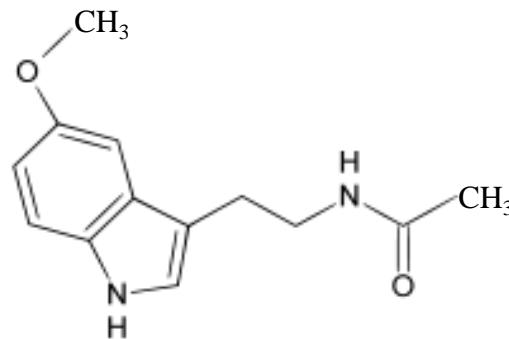


Curved advertisement panel

TBS TV「夢の扉」より

A possible physiological problem

Melatonin :N-acetyl-5-methoxytryptamine



*A hormone with
physiological rhythm adjustment and hypnotic effect
Commercially available as medicine for anti-jet lag but
forbidden in Japan.*

The residue blue radiation of **440-490 nm** used for the excitation of white LEDs has possibility to suppress the hormone secretion (at 464 nm) and to interrupt sleeping.



Adjustment of color temperature to suppress the blue radiation using 3-color LEDs.

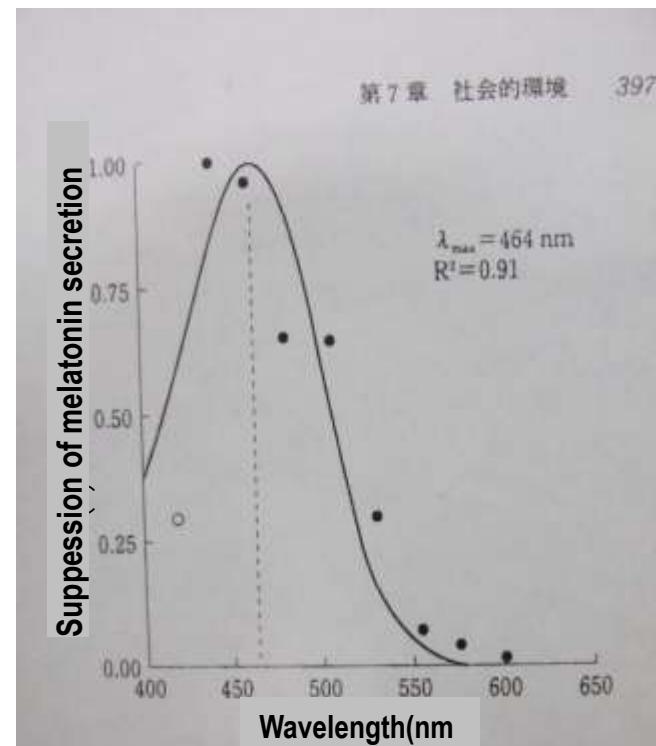
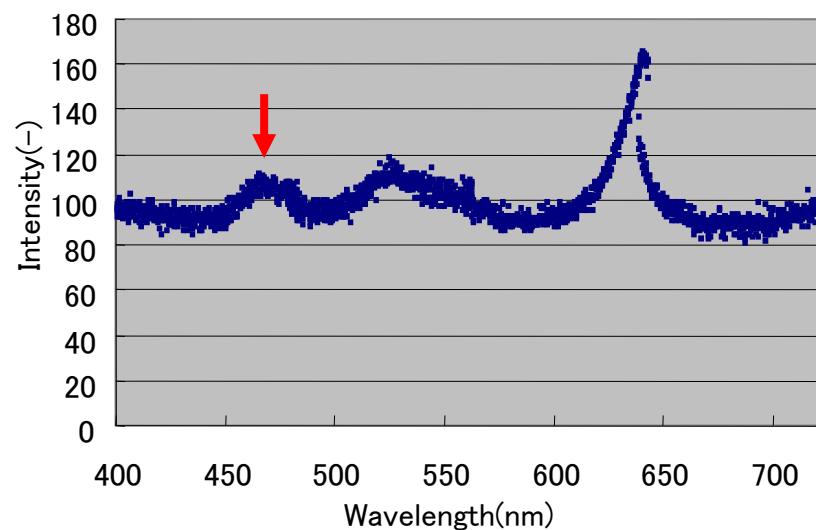


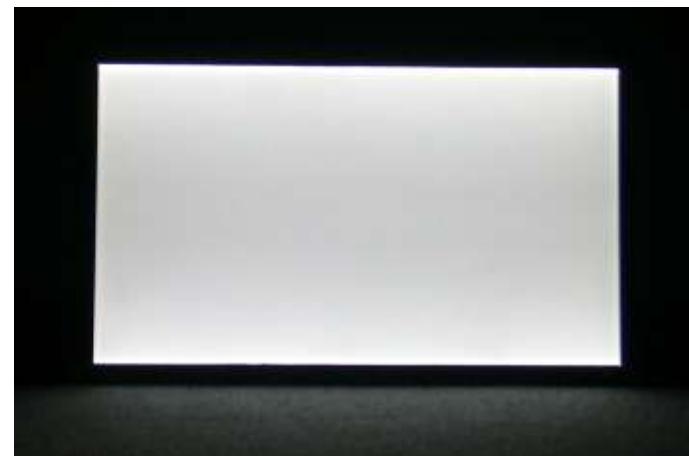
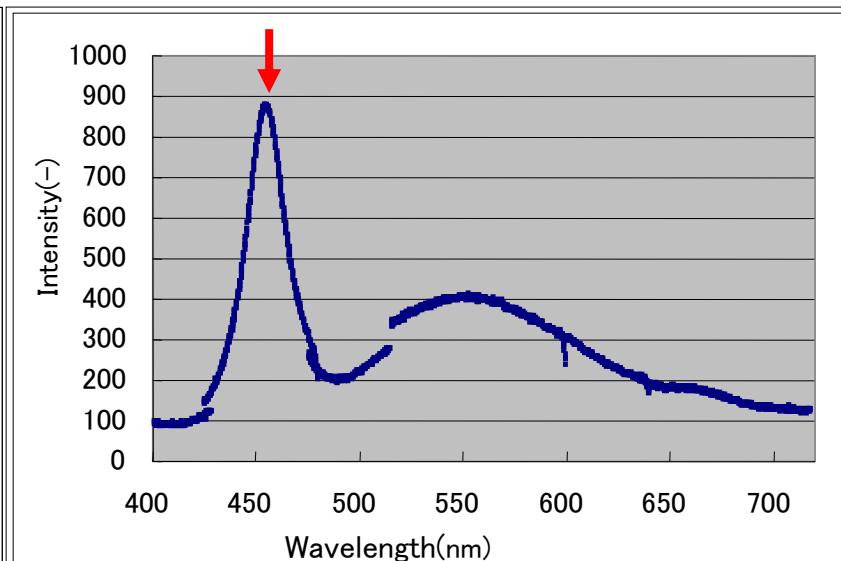
Fig. Effect of wavelength on suppression of melatonin secretion (cf. Brainard t. al., 2001)

Spectra

3 color LED panel at
a color temperature of 2591K
Close to that of W lamps.



White LED panel at 6504 K



エネルギー・システム計測研究時代

- ・ <助教授時代>寺前先生の後任として新井紀夫先生と高温エネルギー・システム・計測研究
- ・ ○名古屋大学高温エネルギー変換研究センター所属（平成6 - 12年）
- ・ <教授時代>
- ・ 分光可視化技術；火炎の可視化とともに、核融合プラズマの温度や密度、湿度の可視化などに成功した。名古屋大学の大野先生やメリーランド大学のGupta先生と共同研究。
○名古屋大学高効率変換研究センター所属（平成12 - 14年）
- ・ ○名古屋大学エコトピア科学研究機構＆研究所所属（平成14 - 25年）





連携先の友人たち

第二の人生 実業と研究や後進の育成、社会科学と芸術の琢磨

○ベンチャーカンパニーと特殊LED製品開発および販売

○アジアの大学においてボランティア講義およびエネルギー・システムを中心とした研究指導

○趣味の研鑽：写真活動、楽器演奏、真空管アンプ、言語、宗教、民族文化、
音楽・舞踊、歴史の再勉強 等々

四十二年の亘り、関係した皆様には、私の我儘を聴いていただき誠にありがとうございました。
また、ご迷惑をかけた方々にはこの場を借りてお詫びを申し上げます。
退職時の研究厄年以後、精一杯生きてゆきます。
また、どこかでお目にかかることができることを楽しみにしております。



芭瑠の里夕陽谷と併に式拾年余生夢観ん楽邦の章



- ・ 奥さま、家族、亡き両親、ありがとう。
- ・ 共著者、学生さん、共同研究の方々など、お世話になった方、数知れず、心からお礼を申し上げます。
- ・ 奉職27年11ヶ月＋学生時代6年間、名古屋大学と皆様ありがとうございました。