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Tetsuo Hadeishi

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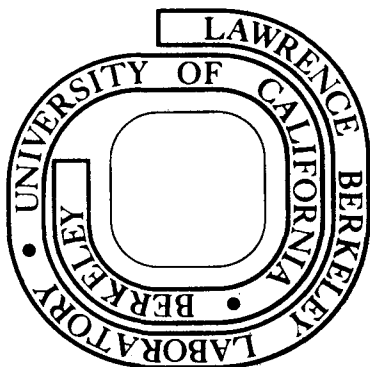
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ISOTOPE SHIFT ZEEMAN TECHNIQUE FOR
DETECTION OF ATOMS AND MOLECULES*

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ABSTRACT

About 4 years ago, researchers at the Lawrence Berkeley Laboratory were encouraged to go into environmental research. As a result, many methods, based on techniques previously developed, evolved that are proven to be of considerable value to environmental monitoring. Isotope shift Zeeman technique is only one of such developments at the Lawrence Berkeley Laboratory. This technique is basically an atomic absorption spectroscopy method. However, there is one basic difference which is unique to this invention. IZAA (Isotope shift Zeeman effect Atomic Absorption) technique is capable of detection of atomic elements directly from the host material without prior chemical treatment. A typical measurement time for most samples is 15 seconds and very seldom exceeds a minute. A brief explanation of the principle of IZAA and the operating characteristics will be presented.

The optical absorption cross section for the resonance absorption by atoms is proportional to the square of the wavelength. Because of the long wavelength in the optical region, say from 2000 to 10 000 Å, the absorption cross section is on the order of 10^{-10} cm². Thus, it is evident that the atomic absorption technique is extremely sensitive compared with other techniques such as x-ray fluorescence and neutron activation. However, the conventional atomic absorption technique is extremely susceptible to the background interference. Many attempts were made in the past to overcome this difficulty. The standard background correction is made by means of dual light beams; one of them is usually a selected portion of the continuum from a deuterium light source and the other from a spectral line source such as a hollow cathode. However, the very fact that two independent light sources were used implies that it is not possible to have the same intensity for extended periods of time. Thus, when high sensitivity is required, it is not possible to accurately balance the light intensity from the two sources (whether the intensity is to be balanced before the optical detector or after the detector by electrical means). The problem gets even more serious when a mechanical chopper is used to alternately allow one or the other beam into the photodetector since it is very difficult to keep the shape and direction of the two beams the same. In the case of IZAA, two groups of wavelengths, one to monitor the atomic vapor and the other to monitor the background, are generated from the same light source and truly a single light beam containing two groups of wavelengths is used. Thus, this technique offers just about the best possible condition for the background correction. Figure 1 illustrates the operating principle of Zeeman effect atomic absorption spectroscopy technique.¹ Figure 2 shows the relationship between the absorption profile of naturally occurring mercury in one atmosphere of nitrogen (STP) and Zeeman triplets of mercury isotope 204 at 2537 Å. The mercury spectral line is generated from the low pressure mercury electrodeless discharge in the magnetic field with almost no self-reversal. The π component is not shifted and is polarized parallel to the magnetic field while the σ components are shifted by the Zeeman effect by $\pm g_J \beta H / h$ from the π component and both are polarized perpendicular to the magnetic field. Thus, the π component is used to monitor the density of atomic vapor while the two σ components are used to monitor the background due to scattering from particulates (smoke) and absorption by molecular absorption band. Because of the polarization property associated with these Zeeman components, the π and σ components can be selected by a linear polarizer. At $H = 15$ kG, the shift in the wavelength is 0.065 Å so that the background attenuation applies equally to all the Zeeman triplet. However, only the π component gets absorbed by mercury vapor. Thus, by means of automatic gain control set in such a way that the output of the photodetector for the sigma components is always constant, the accurate amount of mercury can be determined, since errors arising from scattering and molecular absorption can be accurately corrected.^{2,3}

In the actual instrument, polarization selection, hence, the wavelength selection, was made periodically by means of a magnetically actuated variable-phase retardation plate based on the photoelastic effect.³ Figure 3 shows the operating principle of the instrument with the electro-optical wavelength selection. The host material (sample) is vaporized thermally in the high temperature furnace in presence of oxygen. The instrumental development went through the usual evolutionary steps. Figure 4 shows the original mercury detector used for illustrating the principle of operation; it is currently used by the Environmental Protection Agency in Las Vegas (NERC), Nevada. Figure 5 shows the more recent engineering prototype unit for field use. We have used mercury detection as an example. This principle can be used for almost any element.

So far, we have described the ability of the IZAA technique to correct for background interference. This is not sufficient to measure the amount of trace element accurately. In order to measure trace elements accurately, detection

must be independent of matrix effect. This means we must be able to detect the amount of the trace elements of interest, regardless of the nature of the host material. Thus, whether one is measuring from host materials which are solids, liquids, biological samples, or gaseous samples, the amount of trace elements detected must be independent of the type of host material. This is accomplished by the design of the absorption furnace. Figure 6 shows the basic configuration of the furnace used. A detailed mathematical model describing the operation of the furnace was made. With the configuration of the furnace shown in Fig. 6, it is evident that as long as the additional flow rate due to the sample evaporation does not vary the flow rate of the carrier gas (usually oxygen), matrix effects do not exist. This condition is easily satisfied by flowing a sufficient amount of carrier gas. The matrix independence was tested by intercomparison of the measurements made by IZAA with other methods such as wet chemistry, neutron activation, and x-ray fluorescence. This is shown in Table I for mercury.

Figure 7 shows the linearity and the range of the instrument for Hg. Figure 8 shows the reproducibility for various type of samples. Figure 9 illustrates the capability of the instrument for detection of mercury in human hair, urine, soil, and fish meat. The IZAA instrument in the latest form is capable of detecting Hg, Pb, Cd, and As. The very same instrument should be capable of detecting Sn, Bi, Se. The main limitation for other elements is the temperature range of the present furnace, which goes up to only 1700°C. However, with development of a higher temperature furnace, most elements should be detectable. Also, a graphite rod atomizer which is commercially available can be used until a more satisfactory furnace is developed in the near future.

We shall briefly describe the use of the IZAA technique for detection of molecules. Because of the complex absorption spectra of molecules in the ultraviolet region, most molecular detections are made in the infrared region. However, the photodetection problem in the infrared region is extremely severe because of low quantum efficiency and the thermal noise. It is evident that if we could find a way to detect molecules in the ultraviolet region, the detection problem could be greatly simplified. In order to detect molecules in the ultraviolet region by using the IZAA technique, we have treated the vibration band associated with the optical transition in the same way as the absorption line of atoms. In order to achieve a similar background correction scheme used in atomic detection by IZAA, we used the self-reversal effect of the light source at the resonance lines. Consider, e.g. the 2980 Å resonance line of Cd in a magnetic field. Similar to the mercury resonance line, we again have the Zeeman triplet for the even isotopes of Cd. If we let such a line pass through a Cd absorption cell in zero magnetic field, the unshifted π component is completely absorbed while all the σ component pass through, provided the magnetic field in the light source is sufficiently high. On the other hand, all of the non-resonant lines pass through the Cd vapor cell. It so happens that the 2980 Å line of Cd coincides almost exactly with one of the optical vibration band heads of SO₂ and the nonresonant 3080 line lies between absorption bands of SO₂. Thus, by switching σ components of Cd at 2980 Å on and off by an electro-optical switch and using the 3080 line as a reference monitor, we have exactly the same condition as atomic detection using the IZAA technique. There are many similar coincidences with other resonance lines of Cd as well as other resonance lines of Pb and As. By this technique and by the use of a folded mirror configuration to achieve a path length of about 10 meters, about 10 ppb of SO₂ can be detected. Also, this technique is not limited to SO₂ but other molecules can be detected in a similar way. At present, we are concentrating our efforts on the detection of SO₂, CO, CO₂ and the identification of sulfates and nitrates.

We believe that our research, which led to the development of IZAA, has demonstrated that this technique could be quite universally used for the detection of many elements directly from the host material without the usual requirement of chemical pretreatment. We also believe that we have just touched

the surface of the capability of this type of technique. As time progresses, it is possible that many exciting developments for the detection and identification of molecules will result from this work.

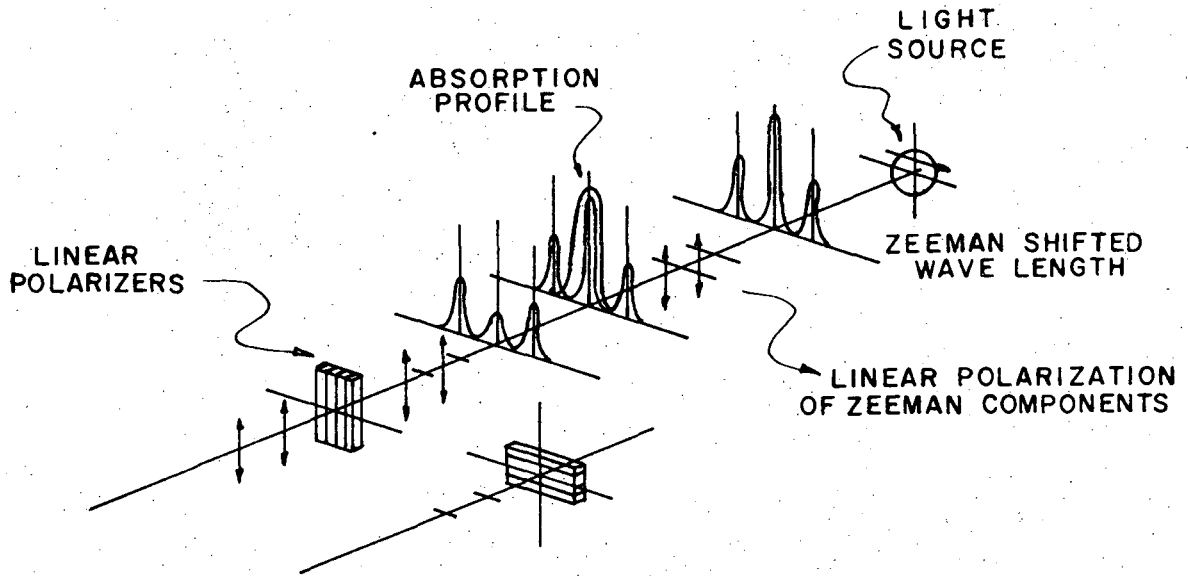
Footnote and References

* Research funded by RANN division of NSF and the U. S. Atomic Energy Commission.

1. T. Hadeishi, patent No. 3811778 assigned to the U. S. Atomic Energy Commission.
2. For an explanation of the role of AGC, see T. Hadeishi, *Appl. Phys. Lett.* 21(9), 438 (1972).
3. T. Hadeishi, D. A. Church, R. D. McLaughlin, B. D. Zak, and M. Nakamura, Total Mercury Monitor for Ambient Air: The IZAA Spectrometer, LBL-1593 (1973).

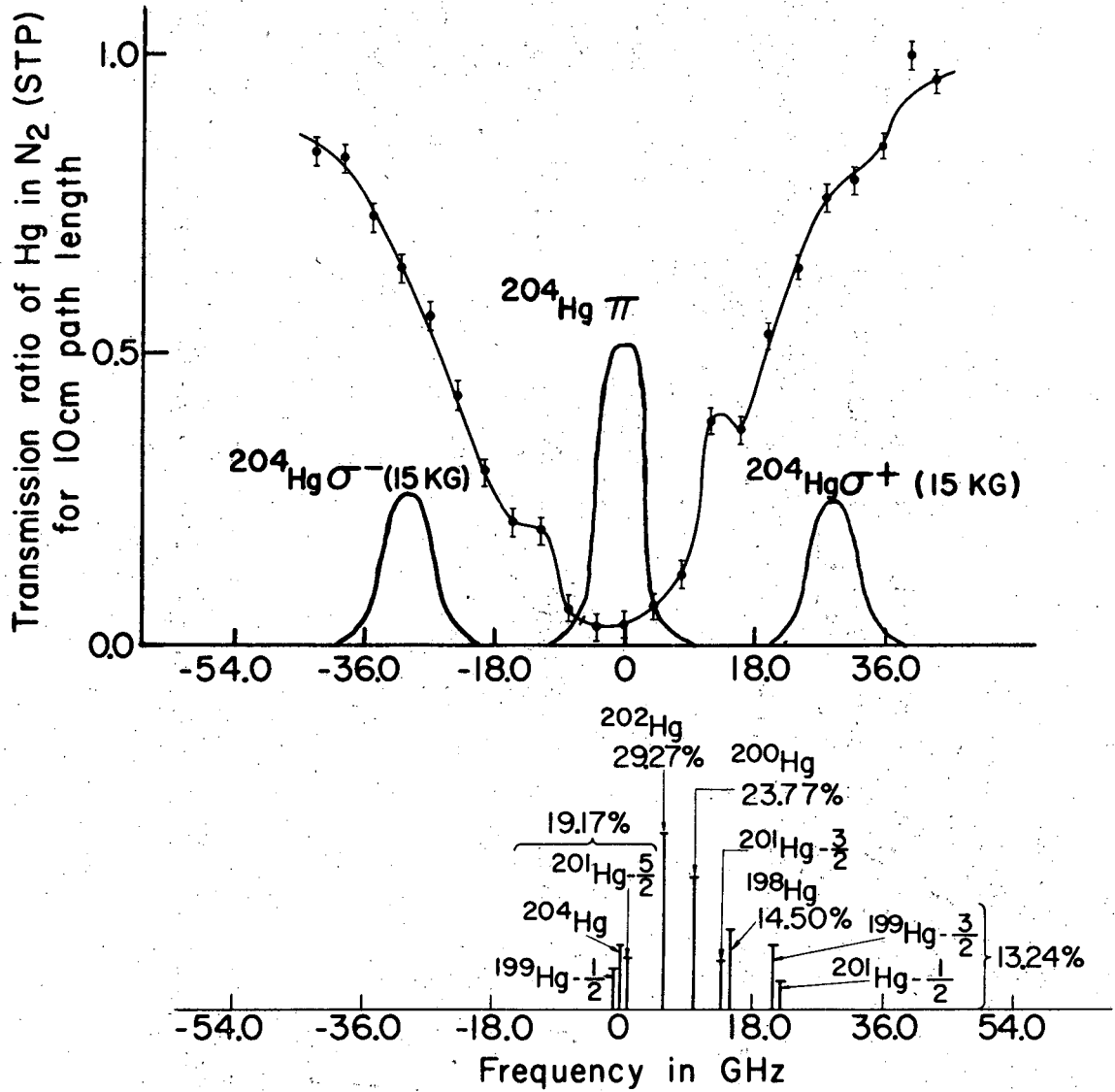
Figure Captions

- Fig. 1. Explanation of IZAA principle.
- Fig. 2. Relationship between Hg atomic absorption at 2537 Å in N₂ (STP) for 10 cm path length and Zeeman effect at 15 kG magnetic field.
- Fig. 3. Block diagram of the instrument with an electro-optical switch for alternatively selecting σ and π components.
- Fig. 4. First IZAA demonstration unit.
- Fig. 5. The applied research prototype IZAA.
- Fig. 6. Basic configuration of furnace.
- Fig. 7. Illustration of linearity and range.
- Fig. 8. Illustration of reproducibility.
- Fig. 9. IZAA mercury detection in various host materials.



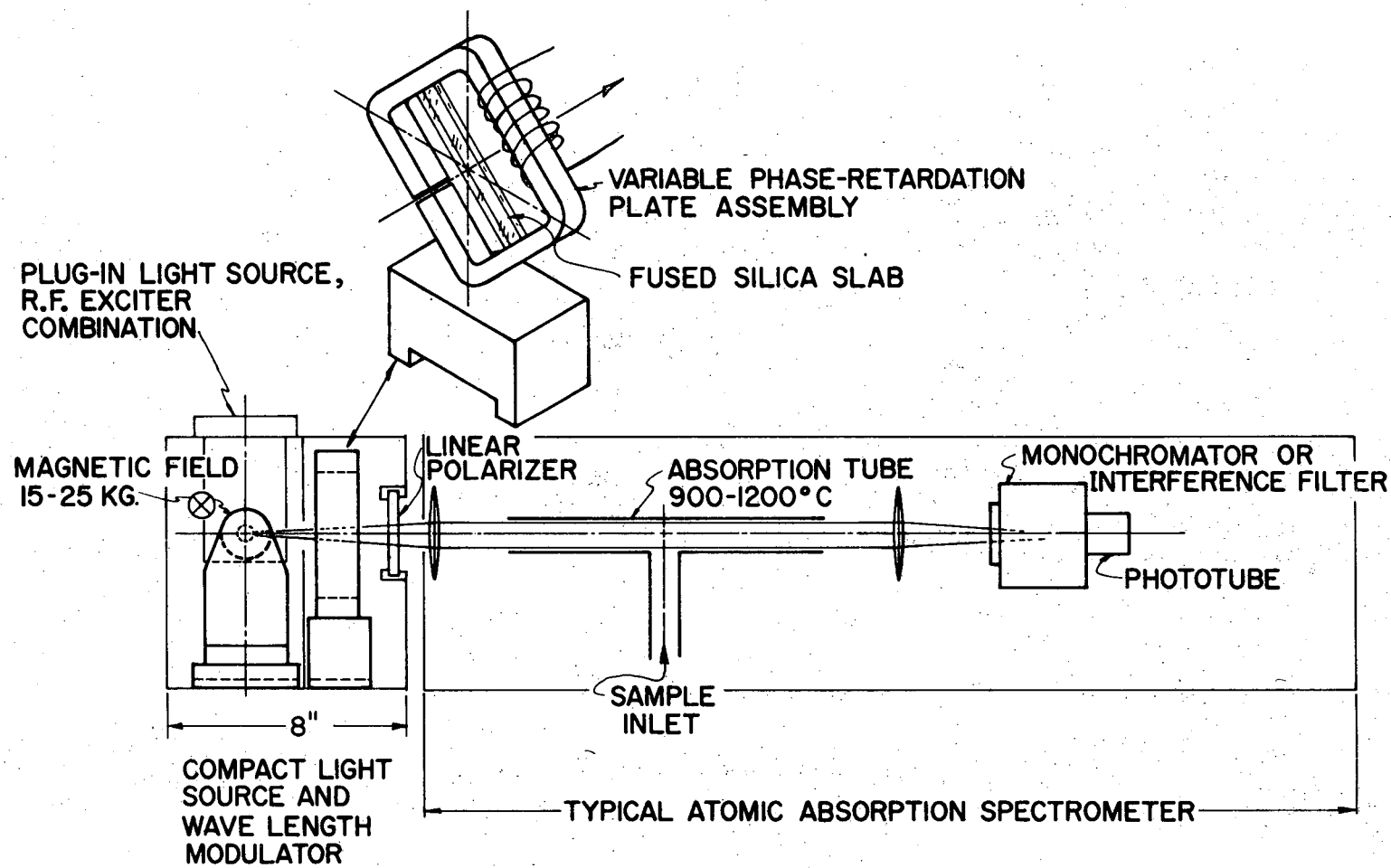
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Fig. 1



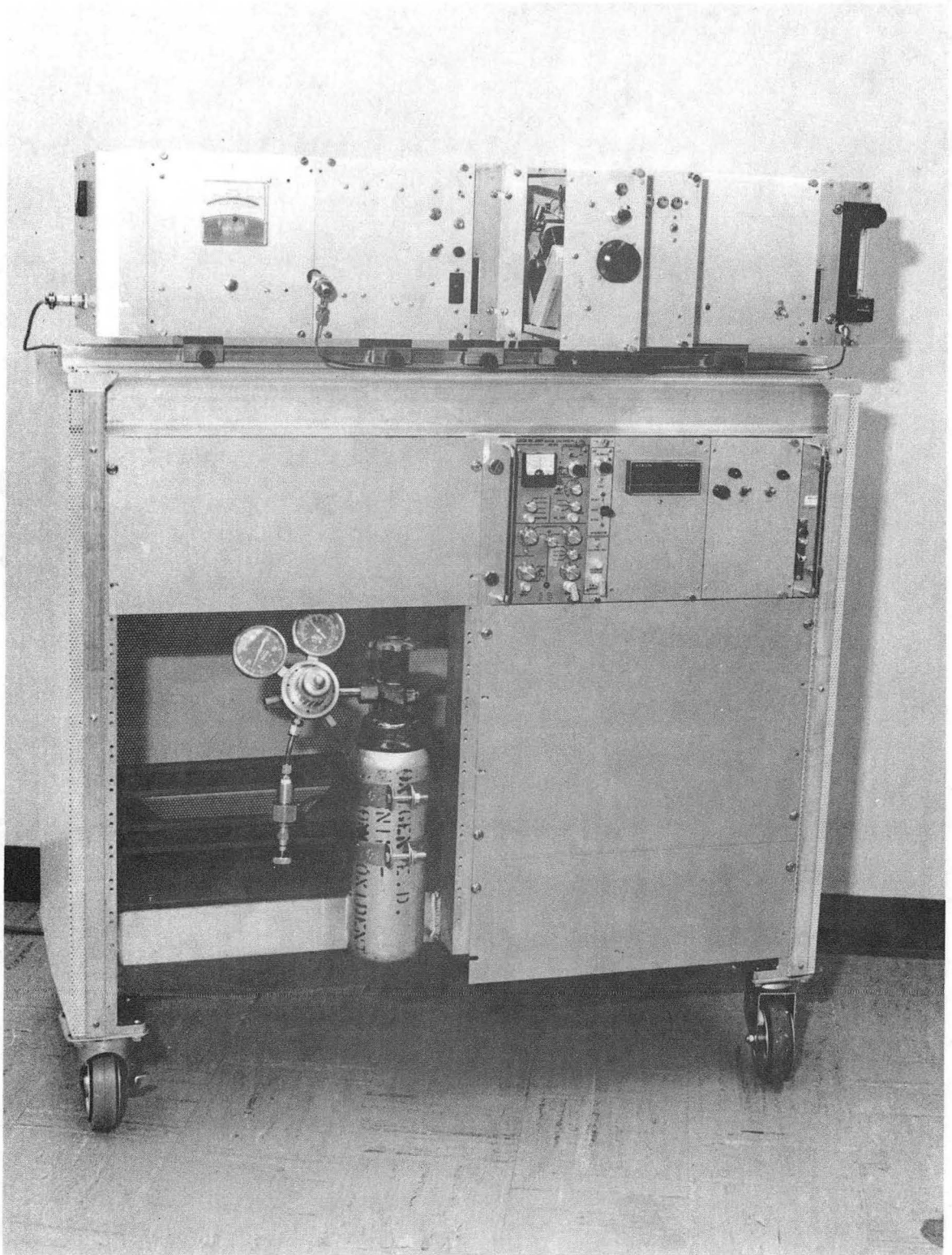
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Fig. 2



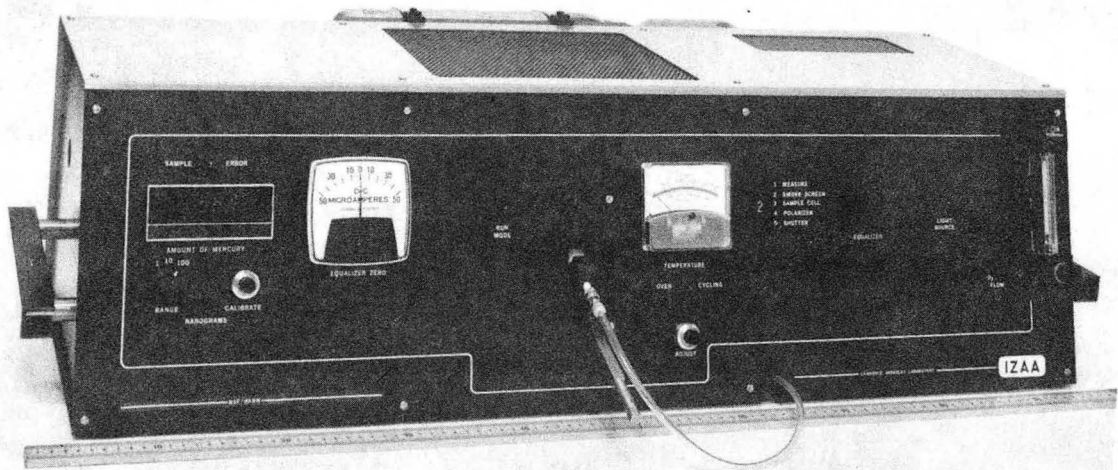
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Fig. 3



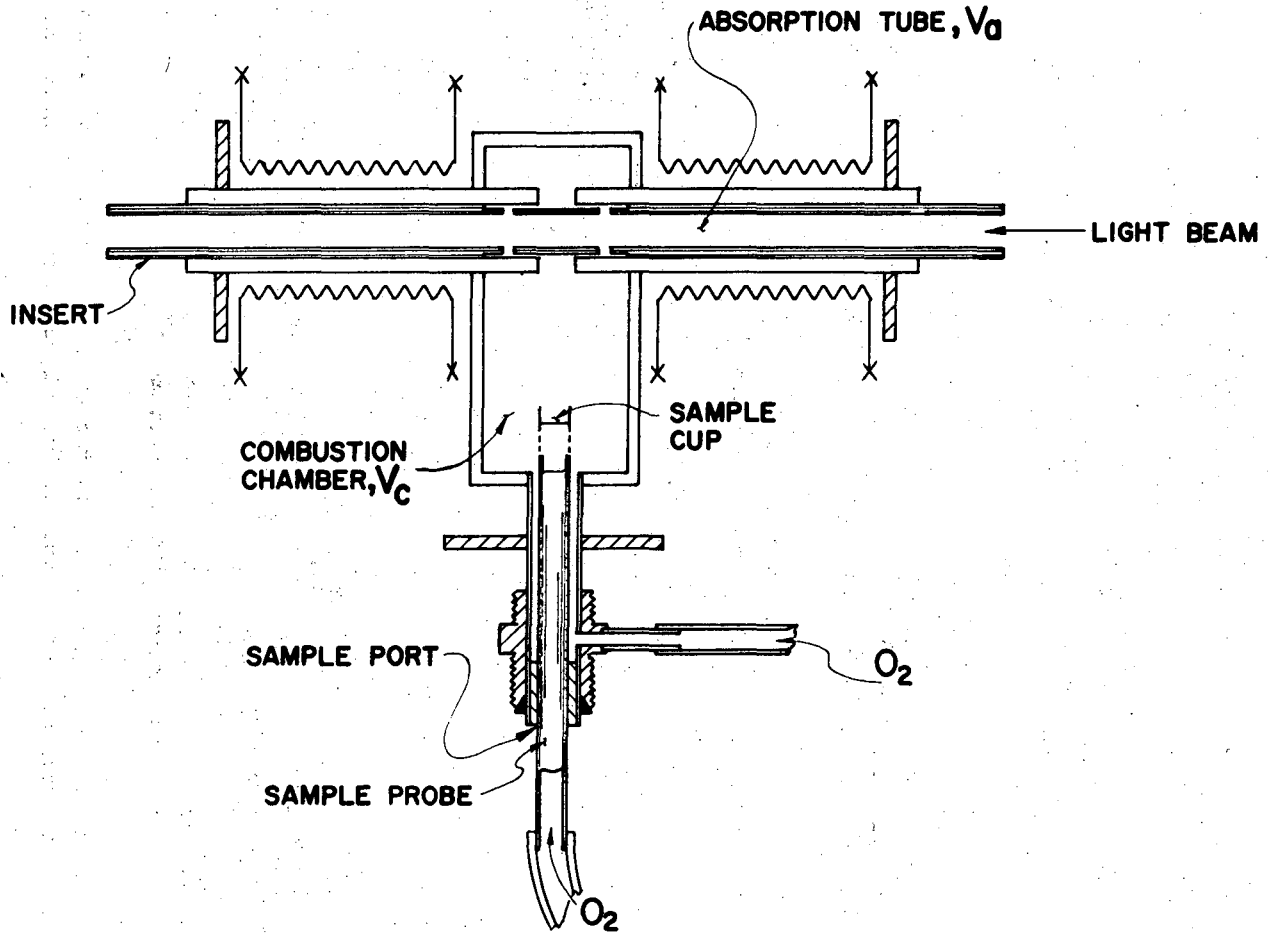
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Fig . 4



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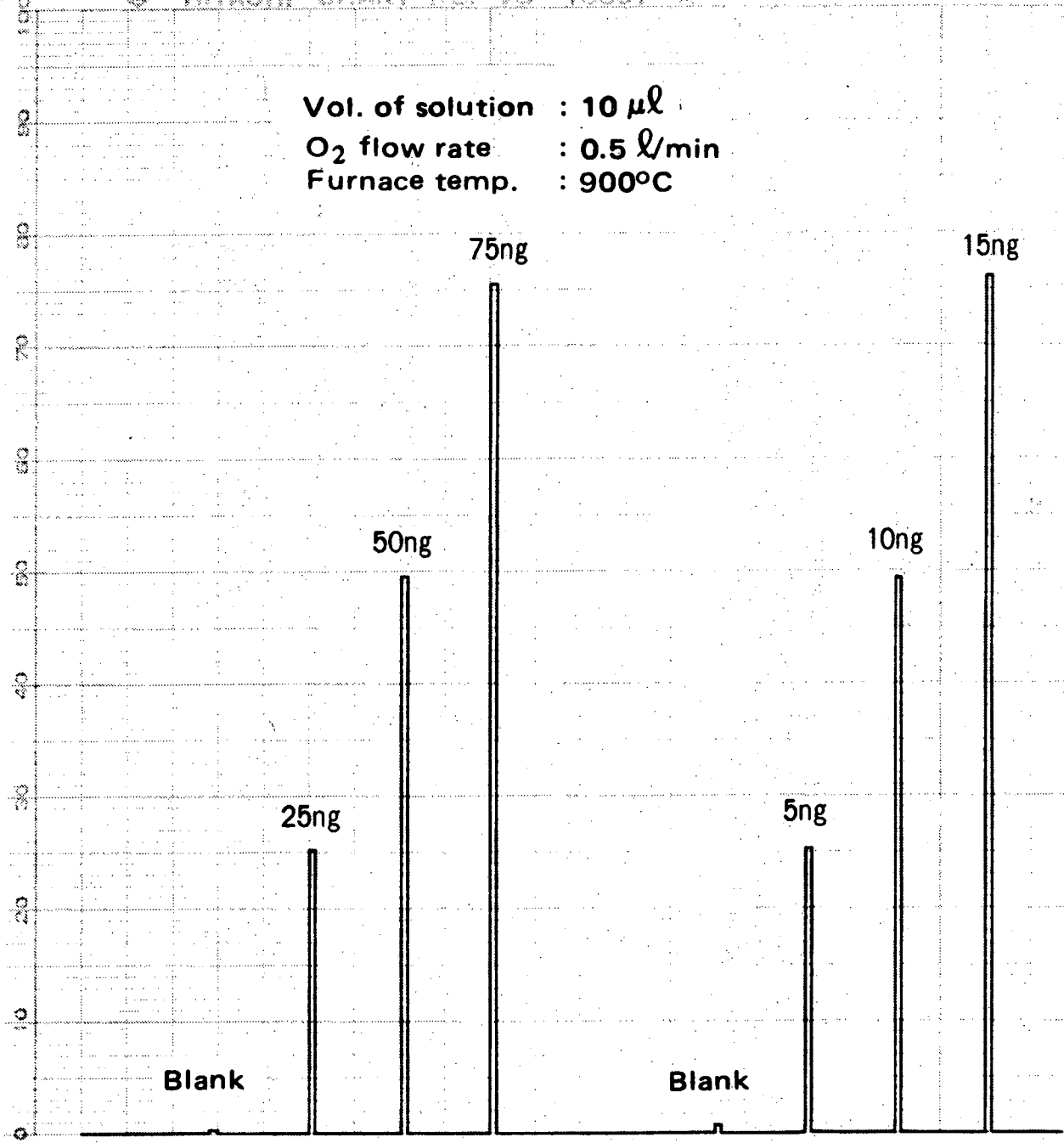
Fig. 5



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Fig. 6

Vol. of solution : 10 μ l
O₂ flow rate : 0.5 l/min
Furnace temp. : 900°C

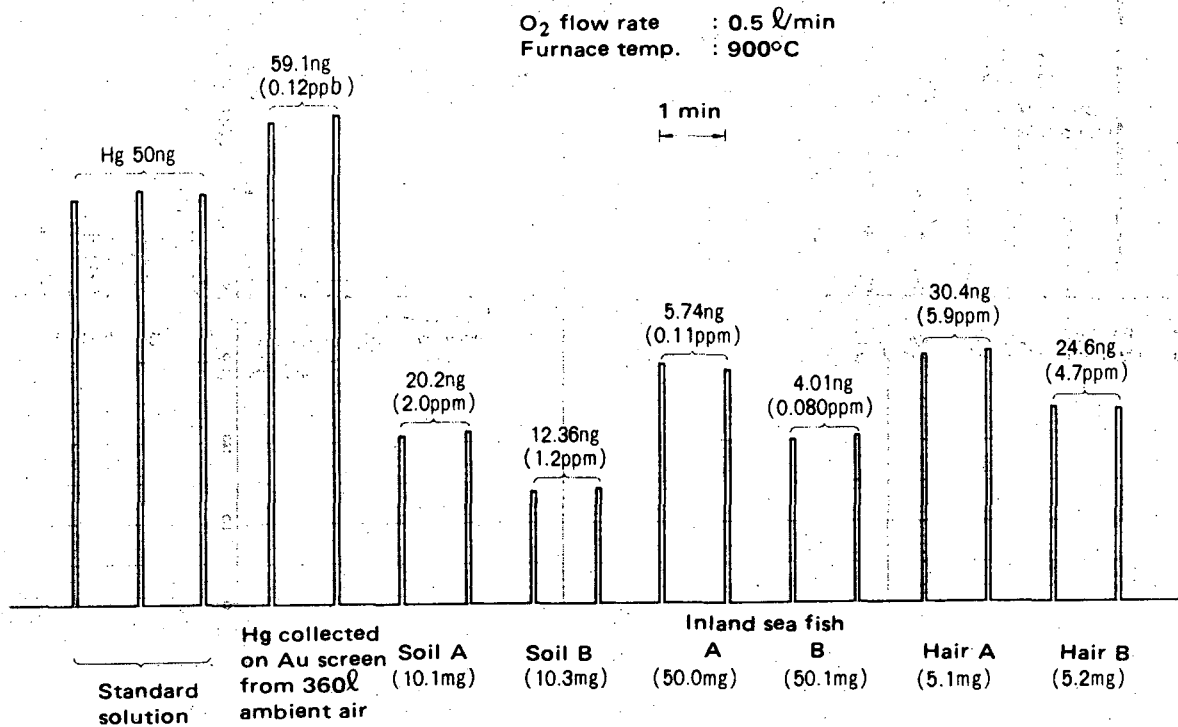


0-100 ng scale

0-20 ng scale

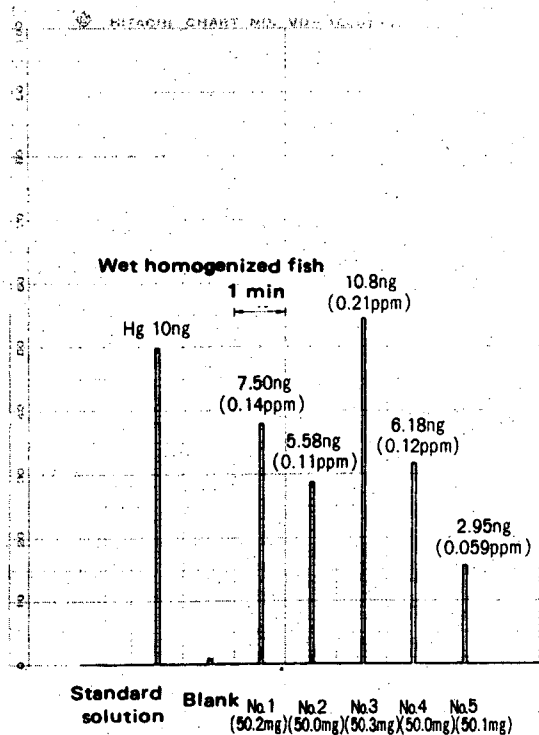
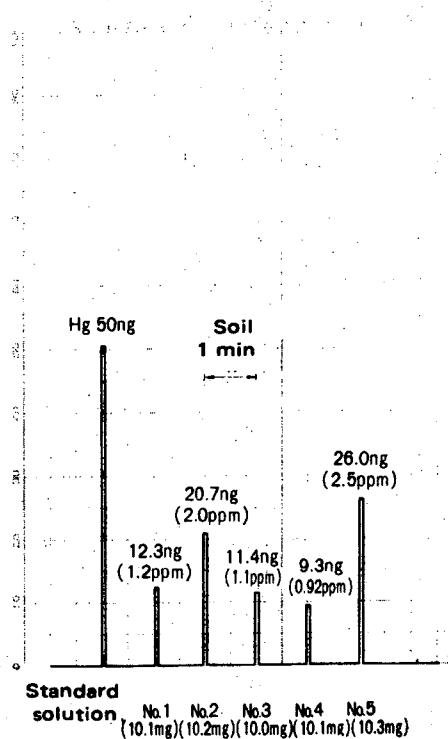
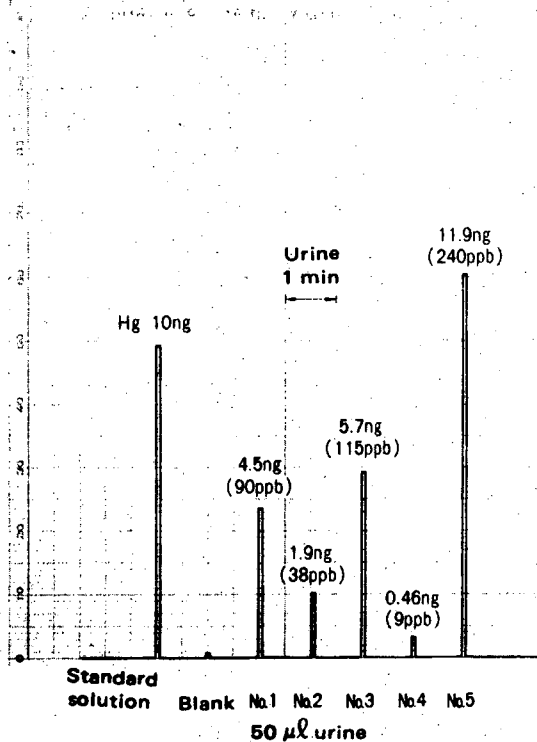
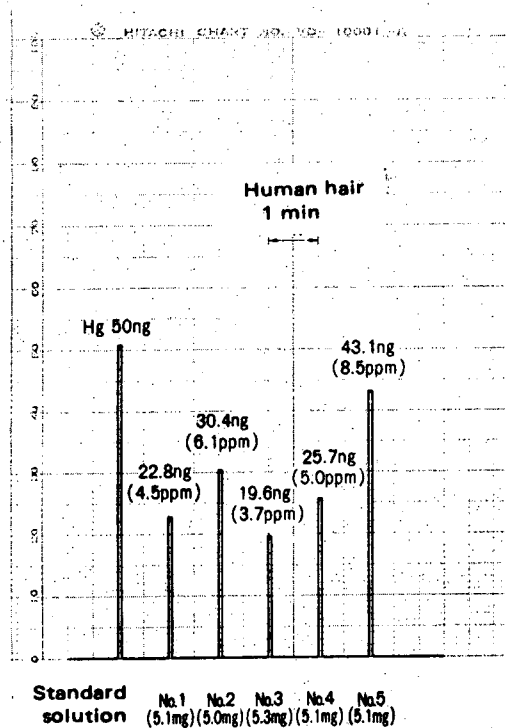
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Fig. 7



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Fig. 8



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Fig. 9

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