Low-Cost, High-Performance Sample Cell for X-Ray Spectroscopy of Solutions and Gels Made from Plastic Straw

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Abstract

Low-cost tube-type sample cells for X-ray spectroscopy of solutions, sols, and gels were made from plastic straws. Energy-dispersive X-ray fluorescence (XRF) experiments showed that the X-ray transparency of the straw cells is ~50% superior to that of quartz capillary cells for 6–7 keV XRF and is almost uniform over the entire range, allowing its use for position-dependent measurements. Wavelength-dispersive XRF experiments showed that the difference in the surface curvature between the straw cells and pellet samples leads to an apparent ~1.5 eV shift of the Fe Kβ1,3 peak; however, chemical effects of Fe Kβ1,3 spectra can be studied if all the samples (including standards) are evenly set in the straw cells. Additionally, the application of the straw cell in studying precipitation band formation in gels was shown on two gel samples containing 0.004 M [Fe(CN)₆]³⁻/[Fe(CN)₆]²⁻ in 2 mass% κ-carrageenan and 0.040 M Fe²⁺/Fe³⁺ in 1 mass% agarose, respectively.

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Introduction

The interest in self-organized pattern formation via precipitation reactions coupled with diffusion in gels/solutions has recently resurfaced,\(^1\)\textsuperscript{−}\(^5\) partially because of its relevance in micro- and nanotechnology.\(^6\)\textsuperscript{−}\(^8\) The concentration distribution of each element and the chemical states of the locally formed species are indispensable pieces of information for thorough understanding of these pattern formation processes. The combined use of X-ray fluorescence (XRF) spectroscopy and X-ray absorption near-edge structure (XANES) spectroscopy was experimentally proven to be useful for obtaining such in-situ, elemental-selective information,\(^9\) particularly for self-organized, discrete precipitation banding of Prussian blue analogs (PBA) in water-glass gels.\(^10\)\textsuperscript{−}\(^15\)

In previous X-ray spectroscopic studies on self-organized systems,\(^9\)\textsuperscript{−}\(^15\) quartz capillary tubes have been employed as sample cells. These have also been widely used for X-ray diffraction measurements of protein, liquids, liquid crystals, and single crystals and powder specimens that can be degraded by air and moisture. Furthermore, the usage of quartz capillary cells has been reported in experiments on small-angle X-ray scattering of colloidal solutions\(^16\) and inelastic X-ray scattering of molecular liquids.\(^17\)\textsuperscript{,}\(^18\) The main reason for their wide use in X-ray measurements is their high transparency (or low absorption) of their thin wall (\(\sim\)10 \(\mu\)m) for X-rays. Such extremely thin walls, however, make the capillary tubes fragile, despite the capillaries having been employed in elevated pressure experiments of up to 100 bar,\(^19\) and they increase the manufacturing cost.

In this study, we propose tube-type cells as an alternative to quartz capillaries for X-ray analyses of solutions, sols, gels, and reaction-diffusion (RD) processes in hydro-gels. The alternative cells are made of 4 mm-wide plastic straws. Compared to quartz capillary cells, the cells (termed “straw cells” hereafter) are much less fragile, allow for easy introduction of
viscous samples into them, show higher and uniform X-ray transparency, and can be made at a much lower cost. Finally, the reusability of the plastic straws might contribute to alleviating the burden of plastic debris in the environment (e.g., see Ref. 20).

Experimental

Preparation of straw cells

First, a plastic straw was cut 10 mm from the top, and the 10 mm piece was pinched by fingers (Fig. 1a). Second, the pinched piece was put on a hot stirrer seated by a 25 μm-thick Kapton film, and the remaining part of the straw was placed vertically on the pinched piece at ~120 °C. The piece was gradually melted in ~5 s to form the flat bottom of the straw cell (Fig. 1b). Third, the runover parts of the pinched piece were cut, and the length of the cell was adjusted to 80 mm (Fig. 1c). Finally, a sample (solution, sol, or powder) was introduced into the straw cell and was closed by a 3 mm-wide, 12 mm-long styrene-resin stopper covered by Teflon (Fig. 1d).

Chemicals

κ-carrageenan and analytical reagent-grade MnSO₄·6H₂O, Fe powder, α-Fe₂O₃, FeCl₂·4H₂O, FeCl₃·6H₂O, Fe(NO₃)₃·9H₂O, K₄[Fe(CN)₆]·3H₂O, K₃[Fe(CN)₉], and CoCl₂·6H₂O were obtained from Wako Pure Chemical Industries, Osaka, Japan. Agarose for electrophoresis (gel strength, 1800–2300 g/cm³) was purchased from Kanto Chemical, Tokyo, Japan. These were used without further purification. All aqueous solutions were prepared using deionized water.
Preparation of gel samples

Two gel samples, herein referred to as “Gel-1” and “Gel-2,” were prepared as follows. At ~98 °C, 0.60 g κ-carrageenan was dissolved in 30 mL deionized water with vigorous stirring to prepare 2 mass% sols. Then, appropriate amounts of $\text{K}_3[\text{Fe(CN)}_6]$ for Gel-1 and $\text{K}_4[\text{Fe(CN)}_6]\cdot3\text{H}_2\text{O}$ for Gel-2 were added, and the sols were stirred continuously for 30 s to prepare 0.004 M $[\text{Fe(CN)}_6]^{3-}$ and $[\text{Fe(CN)}_6]^{4-}$ inner electrolyte sols, respectively. The resultant sols were transferred to the straw cells using a Pasteur pipette and cooled down in a refrigerator at ~0 °C for ~600 s. The inner electrolyte sols solidified to gels within 600 s. Their height in the straw cells was ~30 mm.

Similarly, at ~98 °C, 0.30 g agarose was dissolved in 30 mL deionized water with vigorous stirring to prepare 1 mass% sols. Then, appropriate amounts of $\text{FeCl}_2\cdot4\text{H}_2\text{O}$ for Gel-1 and $\text{FeCl}_3\cdot6\text{H}_2\text{O}$ for Gel-2 were added and stirred continuously for 30 s to prepare 0.040 M $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ outer electrolyte sols, respectively. The resultant sols were poured over the inner electrolyte gels using a Pasteur pipette and cooled down at ~25 °C. The outer electrolyte sols solidified to gels within 600 s. Their height in the straw cells was ~20 mm. After solidification of the outer electrolyte gels, ~0.06 mL of deionized water was poured on top of the gels to prevent them from drying and cracking. The straw tubes were then closed with the stoppers (Fig. 1d).

Apparatus and measurements

To check the performance of the straw cell, two types of laboratory-use XRF setups were arranged: energy-dispersive, to monitor position-dependent XRF, and wavelength-dispersive, to examine the chemical effects of $\text{Fe K}_{\beta1,3}$ emission. All measurements were performed at ~25 °C.

The energy-dispersive setup was modified from a setup used previously.$^{14}$ Cu $\text{K}_{\alpha1}$ X-rays
from an 18 kW generator (RU-300, Rigaku, Tokyo, Japan), operated at 40 kV and 40 mA, were used as the excitation source and were focused to within 0.5 mm in the horizontal direction by an SiO$_2$ (10$ar{1}$1) Johansson-type crystal monochromator (Saint-Gobain Crystals, Nemours, France). The rod-like sample placed in the cell was placed perpendicular to the incident X-ray beams with line-shape on a computer-controlled X-Z stage (XA05A-L2, Kohzu Precision, Kawasaki, Japan). The XRF signals from sample were detected using a silicon PIN detector (XR-100CR, Amptek, Bedford, MA), for which the detection angle relative to the incident beam was set to 135°, and were collected for ~90 s by a multichannel analyzer (MCA8000A, Amptek).

The XRF intensity distribution of the samples in the X-direction was monitored by moving the straw cell (or the quartz capillary cells for comparison; Mark-tube, Hilgenberg GmbH, Germany) along the X direction in 1 mm steps. The collection of a complete XRF distribution over 50 mm of the samples took ~4500 s. After subtracting the background from XRF peaks, the integrated intensities of the peaks were used to obtain XRF distributions of the samples. The intensity variation of the incident X-rays was within 2%.

The wavelength-dispersive setup was modified from a setup reported previously.$^{21}$ The Cu K$_{α1}$ X-rays from the generator (operated at 40 kV and 120 mA for standards and 40 kV and 150 mA for gel samples) were focused to within 0.5 mm in the horizontal direction by an Si (400) Johansson-type crystal monochromator (Saint-Gobain Crystals). A slit of $5 \times 7$ mm$^2$ (width × height) was placed ~100 mm in front of the sample to guard from parasitic emissions from the monochromator. The sample was mounted perpendicular to the line-shape X-ray beams on the focal position, and the irradiate position was changed manually.

Fe K$_{β1,3}$ emission from the sample was analyzed by a Ge (620) spherically bent Johann-type crystal (Saint-Gobain Crystals; bending radius, 820 mm; diameter, 75 mm), which had been employed for resonant Fe K$_{β1,3}$ measurements at SPring-8, Hyogo, Japan.$^{22}$
crystal was placed on a Rowland circle so that the detection angles were ~140°. As confirmed later, the employed optical system was sensitive to the position and the surface shape of light-emitting area. An evacuated beam path (with 50 μm-thick Kapton windows) was set in front of the analyzing crystal to avoid the absorption and scattering of X-rays by air. The energy resolution of this setup has previously been estimated at 0.6 eV.21,22

Highly resolved Fe Kβ1,3 spectra were measured over the emission energies of 7.050–7.065 keV in 0.5 eV steps by rotating the analyzer crystal and linearly moving a XR-100CR detector simultaneously. The typical collection of the Fe Kβ1,3 spectra took ~3 and ~12 h for standards and gel samples, respectively.

Results and Discussion

Straw cell properties

First, the ease and cost of preparing the straw cells (Fig. 1) must be emphasized. Preparing a straw cell is currently ~1000 times cheaper than purchasing a 4 mm-wide quartz capillary (~10 JPY ≈ 0.09 USD vs. ~10,000 JPY ≈ 91 USD). Furthermore, the high workability of plastics allows for easy adjustment of the length of the cell, depending on the sample quantity.

Second, the straw cells were resistant to physical impact, e.g., they were not broken by falling from an ~1 m-high table, unlike the quartz capillaries, which is important in handling small-quantity and/or high-price samples.

Third, importantly for studies on colloidal and biological materials, the straw cell allowed for easy introduction of viscous sols and solutions (compare Figs. 2a and b).

The drawbacks of the straw cell are relatively low resistance to chemicals, heat, cooling, and pressure. Thus, quartz capillaries are still preferable when using organic liquids, highly
acidic or basic solutions, very high- or low-temperature/pressure samples, and air-sensitive samples that need evacuation.

*Position-dependence of XRF signals in straw cell*

Figure 2c shows the Mn Kα intensity distribution of the 0.10 M aqueous solution of MnSO₄ in the straw cell, measured by the energy-dispersive setup. The observed intensity was constant over the measured region, with a variation of incident X-rays of ~2%. This result demonstrated that the “window” of straw cell is highly uniform for X-rays, and the slight distortion and variation in the thickness are negligible. The straw cell is thus suitable for X-ray experiments in solutions, powders, sols, gels, and position-dependent measurements of RD processes.

*Transparency of XRF signals in straw cell*

Figure 3 compares X-ray emission spectra of the capillary and straw cells with 0.10 M aqueous solutions of MnSO₄, K₃[Fe(CN)₆] or CoCl₂, measured by the energy-dispersive setup. The XRF and scattering (elastic and inelastic (Compton) scattering of Cu Kα) lines from the straw cell were more intense than those from the quartz capillary cell. Because the scattering intensity depends on many factors, it is difficult to specify the cause of the higher intensity in the straw cell. Nevertheless, such higher intensity can be, at least, partially, attributed to the fact that the straw cell consists of lighter elements (mainly H and C) than the quartz cell (O and Si), since the cross-section of Compton scattering of lighter elements is larger than that of heavier elements.

The higher XRF intensity in the straw cell is important in the context of the current study (it is also partially due to the difference in the composition of the cells: *i.e.*, the XRF absorption by lighter elements is lower than that by heavier elements). More specifically, we note that the
integrated intensity of the Mn Kα, Fe Kα, and Co Kα lines from the straw cell were 1.6-, 1.5-, and 1.4-fold higher than that from the capillary cell, respectively. Interestingly, the difference in intensity of the two types of cells slightly decreased as the emission energy increased, namely Mn Kα (1.6) → Fe Kα (1.5) → Co Kα (1.4), possibly due to the attenuation of X-rays by the cell window decreasing as the X-ray energy increased, thus reducing the difference in transparency. In summary, for X-rays of 6–7 keV, the transparency of the straw cell is ~50% superior to that of the quartz capillary.

*Influence of the curved surface of the straw cell in wavelength-dispersive measurements: applicability for chemical state analysis*

The curved surface of the straw cell, as well as of the capillary cell, can shift and/or distort XRF spectra obtained from wavelength-dispersive setups because of the difference in the light-emitting area of curved and flat surfaces by which the focal points differ, thereby giving apparent different Bragg angles for emissions. In fact, high-resolution Fe Kβ1,3 spectra of an Fe pellet and Fe powder in the straw cell (Fig. 4a) indicated that the curved surface of the straw cell led to an apparent peak shift of ~1.5 eV. Such an apparent shift is problematic in chemical state analysis using highly resolved XRF.23,24

Figure 4b shows high-resolution Fe Kβ1,3 spectra of α-Fe2O3, K3[Fe(CN)6], and K4[Fe(CN)6] ·3H2O powder in the straw cells, obtained under the same measurement conditions. As reported in the literature,24 the spectra differed substantially, depending on the chemical environment of the Fe atoms; the Kβ emissions of 3d elements are known to be dominated by the 3p–3d exchange interaction, and are hence sensitive to the spin states of 3d atoms.23,24 The relative peak shifts, which were estimated as the difference between the centers of the Kβ1,3 bands between K3[Fe(CN)6] and K4[Fe(CN)6] ·3H2O (~0.5 eV) and between K3[Fe(CN)6] and Fe2O3 (~1.8 eV), agreed with the values available in the literature (~0.4 and 1.7 eV,
respectively). These findings confirm that the straw cell is applicable in studies of chemical effects, including relative chemical shifts on high-resolution XRF spectra, although their absolute emission energies may be somewhat uncertain due to the curved surface.

High-resolution Fe Kβ₁,3 spectra of 0.50 M aqueous solutions of K₃[Fe(CN)₆], FeCl₃, Fe(NO₃)₃, and FeCl₂ were in agreement with the spectra of each solute powder (Fig. 5), which demonstrated that the Fe Kβ₁,3 profile is less sensitive to distant atoms/molecules, just like XANES. Further, Figure 5b indicates that the Fe Kβ₁,3 spectra of chemical species having octahedral coordination around Fe atoms in high-spin states do not differ significantly, regardless of the coordinated atoms (O or Cl) and the oxidation state (Fe(II) or Fe(III)). This similarity suggests that, for high-spin compounds, the Fe Kβ₁,3 profiles are mostly determined by the atomic 3p–3d exchange interaction and are less influenced by other atoms, even the first nearest neighbors.

In summary, despite possible distortion of the spectra by the curved surface of the straw cell, the differences between Fe Kβ₁,3 spectra of [Fe(CN)₆]³⁻, [Fe(CN)₆]⁴⁻, and the high-spin Fe compounds are clearly distinguishable, suggesting that high-resolution Fe Kβ₁,3 measurements of the PBA samples in the straw cell are potentially usable for chemical state analysis, and hence, for studies on RD processes of PBAs in gels/solutions.

**Examples: Prussian blue precipitation bands formed in organic gels in straw cells**

To confirm the utility of straw cells for studies of precipitation bands of PBA-related materials in gels, we analyzed two gel samples. Figure 6 shows the Fe Kα intensity distribution of the fully developed precipitation bands in Gel-1 and Gel-2 in the straw cell, measured at 523 and 293 h after the addition of the outer electrolyte sols, respectively. The relative XRF intensity, where the Fe Kα intensity at the bottom of the samples in the initial stages (~1 h after the addition of the outer electrolyte sols; not shown here for simplicity), was set to 1, according to
the procedure used in previous studies.\textsuperscript{13-15}

In Gel-1 (Fig. 6a), a peak in the Fe K\textalpha
distribution at the gel boundary ($X \approx 0$ mm), similar to one previously found,\textsuperscript{10} was observed, suggesting Fe accumulation near the boundary. A similar distribution peak was observed in Gel-2, although relatively weak (Fig. 6b). Moreover, the distribution in Gel-1 indicated that, except in the gel boundary (Fig. 6b). Moreover, the distribution in Gel-1 indicated that, except in the gel boundary, Fe species with a considerably uniform concentration were generated over a great portion of the blue band and were diffusive at the region of low concentrations ($X > \sim 18$ mm).

While no significant distribution peak was found for $X < 0$ mm in Gel-1, a considerable distribution band was observed around $X = \sim 6$ mm in Gel-2 (Fig. 6b), suggesting Fe accumulation at the dark-yellow region of Gel-2. In accordance with this, the width of the blue region in Gel-2, as well as of the corresponding Fe K\textalpha
distribution band for $X > 0$ mm, was clearly narrower than in Gel-1, suggesting that high Fe accumulation in the dark-yellow region suppressed the diffusion of Fe ions, possibly aquoiron ions, into the inner electrolyte sols of Gel-2, and, consequently, suppressed the width of the blue band.

High-resolution Fe K\textbeta\textsubscript{1,3} spectra obtained at several positions (top panels in Figs. 6a and b) of Gel-1 and Gel-2, showed noticeable differences, despite the relatively large statistical uncertainties, indicating that the chemical states (spin states) of the Fe species in the gel samples were position dependent. For example, the center of gravity of the 1 mm spectrum was clearly located at the higher energy side than that of the 10 mm spectrum (Fig. 6c). Combined with abovementioned results, this suggests that the concentration of aquoiron ions and/or their related high-spin compounds was relatively high near the boundary of Gel-1, which is consistent with XANES results of similar systems.\textsuperscript{10} Similarly, the center of gravity of the $\sim 6$ mm spectrum showed a considerably higher energy shift than that of the other spectra (Fig. 6d), suggesting the dominance of aquoiron ion-related compounds there (whereas the 0 and 5 mm spectra agreed with each other within experimental uncertainty).
Comparison of the Fe Kβ_{1,3} spectrum of Gel-2 at X = −6 mm with the spectrum of the 0.50 M aqueous solution of FeCl₃ (“Fe (aq) 100%”; Fig. 7a) revealed agreement between the two spectra, which strongly suggests that Fe accumulation around X = −6 mm is not due to the formation of Prussian blue, but due to the polymerization of [Fe(H₂O)₆]³⁺ ions, considering the fact that the color at X = −6 mm is not blue, but dark-yellow, unlike the region for X > 0 mm. Meanwhile, the 0 and 5 mm spectra of Gel-2 agreed with the 10 mm spectrum of Gel-1 within experimental uncertainty (Fig. 7b), suggesting that the chemical states of Fe at these three measuring points were similar, although the preparation conditions for Gel-1 and Gel-2 were entirely different.

Further, the data for these three gels with the linear combinations of the spectra for 0.50 M aqueous solutions of FeCl₃ and 0.50 M aqueous solution of K₃[Fe(CN)₆] were compared in Fig. 7b (note that there is no difference between the Fe(II) and Fe(III) aqueous solutions within experimental uncertainty; Fig. 5b). The Fe (aq) spectrum was weighted by the values in Fig. 7b to add the weighted spectrum of the K₃[Fe(CN)₆] solution, e.g., “Fe (aq) 20%” in Fig. 7b means the averaged spectrum of 0.20 × the FeCl₃ spectrum and 0.80 × the K₃[Fe(CN)₆] spectrum. For the high-energy region (> 1 eV), the “Fe (aq) 0%” spectrum relatively underestimated the spectra of the three gels, the “Fe (aq) 70%” spectrum overestimated them, and the “Fe (aq) 20%” and the “Fe (aq) 50%” spectra overall reproduced the spectra. It can thus be concluded that, at these three areas, [Fe(CN)₆]-related species (possibly due to Prussian blue) were dominant, but coexisted with ~35% of aquoiron ions-related species.

In summary, the following observations demonstrate the utility of straw cells for analysis of the chemical state of Fe compounds in gels and, potentially, for the in-depth understanding of RD processes in gels: the local Fe accumulation near the gel boundaries, the relatively uniform Fe distribution in the blue region of Gel-1, the suppression of Fe diffusion into the inner electrolyte gel by Fe accumulation in the dark-yellow region of Gel-2, the dominance of
[Fe(CN)$_6$]-related species in the blue regions, and the dominance of aquoiron ion-related species in the dark-yellow region of Gel-2.

**Conclusion**

We have made tube-type sample cells from 4 mm-wide plastic straws for application in X-ray spectroscopy of solutions, sols, gels, and RD processes in sample cell. In comparison to quartz capillaries, the straw cells were easy to process and use, low cost, highly transparent for X-rays, allowed for easy introduction of viscous samples into them, utile for chemical state analysis by high-resolution XRF, and useful in XRF analyses of Prussian blue precipitation bands in gels. Straw cells thus provide an alternative to glass capillaries that can be used for a wide array of experiments using X-rays.

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Figure Captions

Fig. 1 Schematic illustration of the process of preparing a sample cell from a plastic straw.

Fig. 2 Straw cell properties. Comparison between (a) a straw cell and (b) a quartz capillary into which a hot sol (~80 °C) prepared from an aqueous solution of 1.2 mass% κ-carrageenan and 0.10 M K₃[Fe(CN)₆] was introduced using a Pasteur pipette. Unlike the quartz capillary, the straw cell allowed for an easy introduction of the sol into it, which then rapidly turned into a uniform gel. (c) Mn Kα intensity distributions of 0.10 M MnSO₄ aqueous solution in the straw cell show its high uniformity.

Fig. 3 X-ray emission spectra of the capillary and the straw cells filled by a 0.10 M aqueous solution of (a) MnSO₄, (b) K₃[Fe(CN)₆], and (c) CoCl₂.

Fig. 4 (a) High-resolution Fe Kβ₁,₃ spectra of an Fe pellet and powder in the straw cell. The peak energy of the pellet sample was set to zero, and the vertical dashed lines serve as a guide. (b) High-resolution Fe Kβ₁,₃ spectra of α-Fe₂O₃, K₃[Fe(CN)₆], and K₄[Fe(CN)₆]·3H₂O powder in the straw cell. The peak energy of the K₃[Fe(CN)₆] was set to zero. In (a) and (b), each peak height was normalized to one, and measured points were connected by straight lines for guides.

Fig. 5 High-resolution Fe Kβ₁,₃ spectra of 0.50 M aqueous solutions of (a) K₃[Fe(CN)₆], (b) FeCl₃, Fe(NO₃)₃, and FeCl₂ in the straw cell. For comparison, the powder data of (a) K₃[Fe(CN)₆], (b) FeCl₂·4H₂O, FeCl₃·6H₂O, and α-Fe₂O₃ are also plotted. The peak energy of the K₃[Fe(CN)₆] powder was set to zero, and each peak height was normalized to one. Measured points were connected by straight lines for guides.
Fig. 6 Fe Kα intensity distribution of the fully developed bands of the (a) Gel-1 and (b) Gel-2 samples in the straw cell. Captured images are displayed at the top of the figures to facilitate a comparison of the Fe Kα distributions with the position of the precipitation bands. The positions at which the high-resolution Fe Kβ₁,₃ spectra of the (c) Gel-1 and (d) Gel-2 samples were recorded are also shown. In the high-resolution spectra (c and d), the peak energy of the K₃[Fe(CN)₆] spectrum was set to zero (see Figs. 4 and 5), and each peak height was normalized to one. Measured points were connected by straight lines for guides.

Fig. 7 Comparison of the high-resolution Fe Kβ₁,₃ spectra between the gel samples (Fig. 6) and standard samples (Fig. 5). The “Fe (aq)” represent the high-resolution spectra of the 0.50 M aqueous solutions of FeCl₃. In (b), the Fe (aq) spectrum was weighted by the values in the figure to add the weighted spectrum of the 0.50 M aqueous solution of K₃[Fe(CN)₆]. For example, the “Fe (aq) 20%” means the average spectrum of 0.20 × FeCl₃ data and 0.80 × K₃[Fe(CN)₆] data. Measured points were connected by straight lines for guides.
Fig. 1
Fig. 2

(a) Straw cell
(b) Capillary cell

(c) MnSO₄ 0.10 M solution

Count rate / cps

Relative position / mm
Fig. 3
Fig. 4
Fig. 5
Fig. 6
Fig. 7