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Evaluation of the Quantitativeness of CNLSD by Using the NMIJ Certified Reference Material Poly(ethylene glycol)

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Introduction

- Poly(ethylene glycol) (PEG) is one of the most important water-soluble polymer, however the determination of its molecular mass fractions are not so easy because it does not have the UV absorbance. Usually, evaporative light scattering detector (ELSD) is used for the detection of PEG, however the quantitativeness of ELSD is so poor that the molecular mass distribution can’t be accurately determined.
- Here, we connected the condensation nucleation light scattering detector (CNLSD) to supercritical fluid chromatography (SFC) and evaluated its quantitativeness using a certified reference material PEG (NMIJ CRM 5006a) with the averaged its molecular mass of 1000.

Conditions of SFC

- **SFC instruments:**
  SUPER-201,
  JASCO Co., Tokyo

- **Detector:**
  ELSD or CNLSD

Table 1 Separation conditions of SFC

	SFC Conditions
Column	SFCpak SIL-5 (4.6 mm × 250mm)
Pressure	200 kg/cm^2
Flow Rate of CO_2	2.0 ml/min
Flow Rate of Modifier	0.6 – 1.4 ml/min (0 – 120 min)
Modifier	MeOH / H_2O (9/1)
Column Temperature	50 ° C
Sample Size	70 mg/ml × 5 μl in MeOH

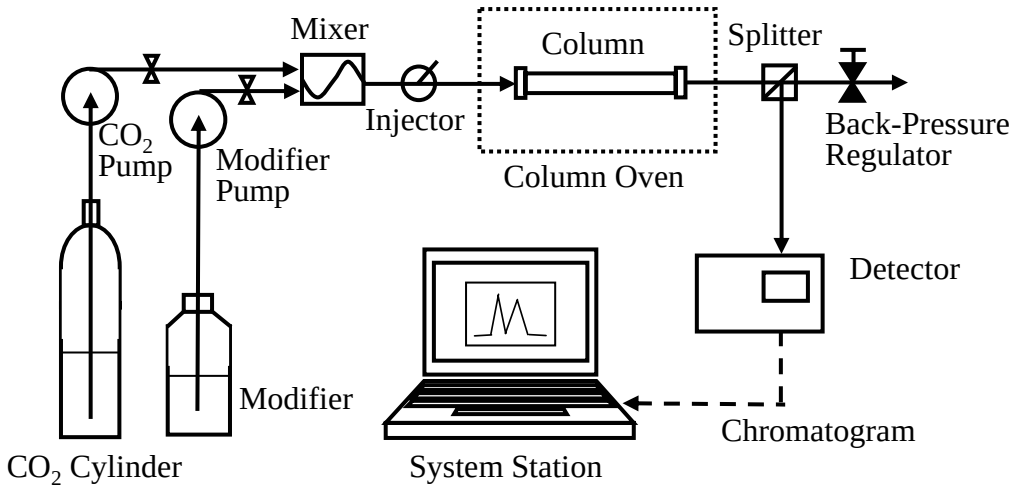

Figure 1 Instruments of SFC

Conditions of CNLSD

- **Spitted SFC eluate are inserted to the CNLSD**

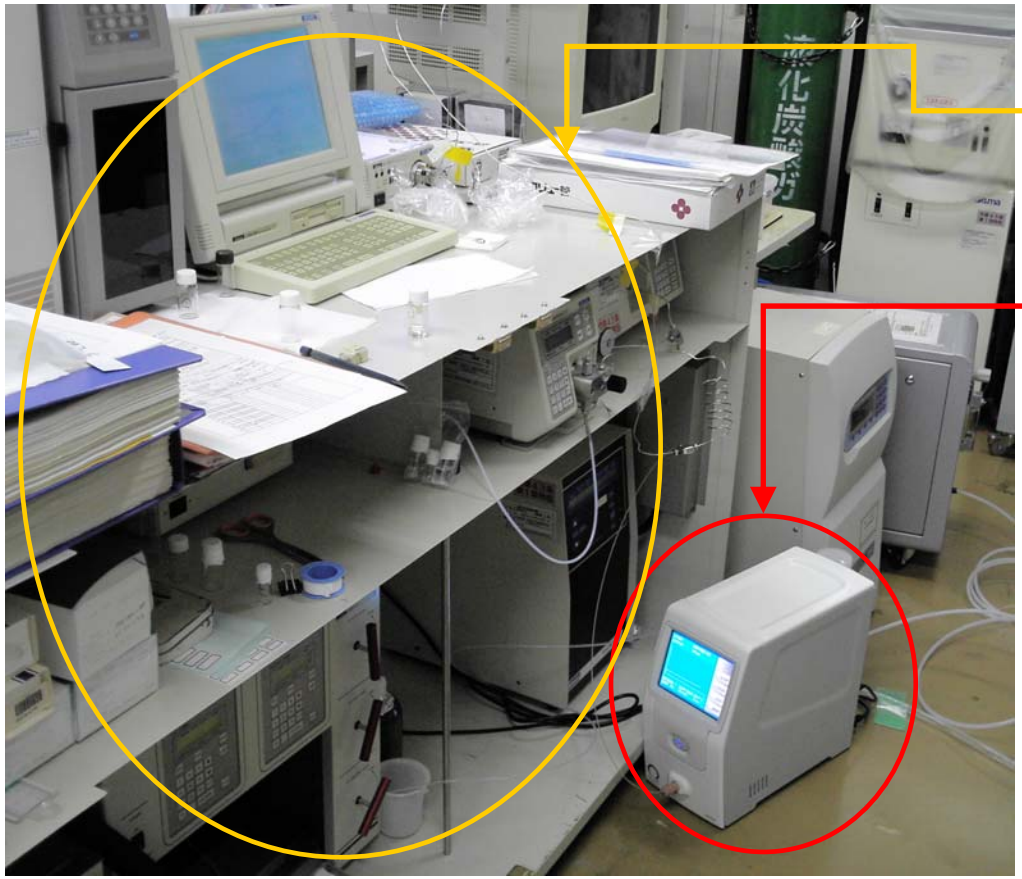

Table 2 Measurement conditions of NQAD

	CNLSD Specifications
Tube Temperature	70 - 90 ° C
Nebulizer Gas	Compressed Nitrogen
Gas Flow Rate	4.7 L/min
Gas Press	30 ± 3 psi

Sample

- **NMIJ Certified Reference Material poly(ethylene glycol) 1000**
- **All containing fractions of poly(ethylene glycol) are certified as well as averaged molecular weights.**

Poly(ethylene glycol) 400 ; CRM No. 5005-a
Poly(ethylene glycol) 1000 ; CRM No. 5006-a
Poly(ethylene glycol) 1500 ; CRM No. 5007-a

- **The appearance of NMIJ CRM, PEG 1000**

References

[1] Rapid Commun. Mass Spectrom, *15-4*, 277-282, 2001
[2] KOBUNSHI RONBUNSHU, *58-10*, 541-542, 2001
[3] J. Mass Spectrom, *38-9*, 948-954, 2003
[4] J. Chem. Phys, 122-24, 244914-1 244914-7, 2005
[5] Int. J. Mass Spectrom, 247-1-3, 85-92, 2005

A Typical Chromatogram of PEG 1000 by CNLSD

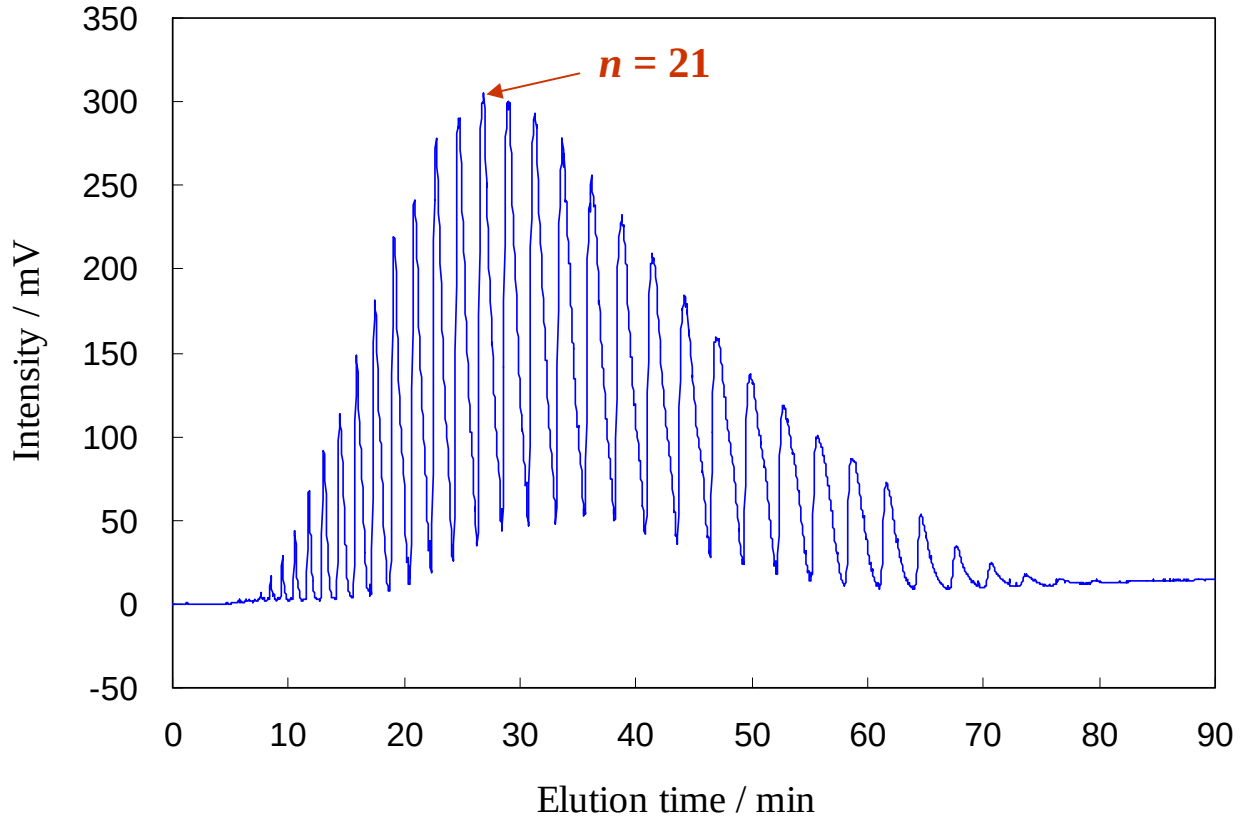

Figure 2 A SFC chromatogram of PEG 1000 by the CNLSD under the conditions listed in Table 1 and 2.

Evaporator Temp. Dependence of CNLSD

- **High evaporator temperature gives large peak areas in spite of getting higher noise levels.**

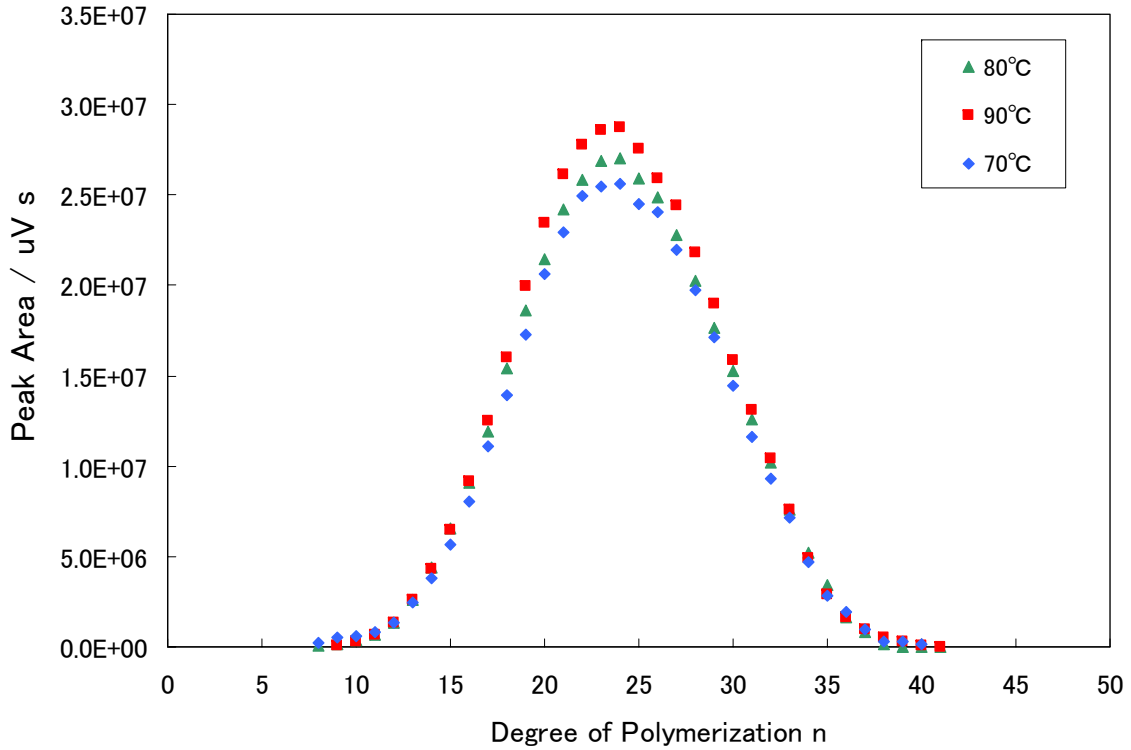

Figure 3 Evaporator temperature dependence of the CNLSD measured by using NMIJ CRM PEG 1000.

Concentration Dependence of CNLSD and ELSD

- **Sensitivity of CNLSD for dilute PEG is about 10 times better than that of ELSD.**

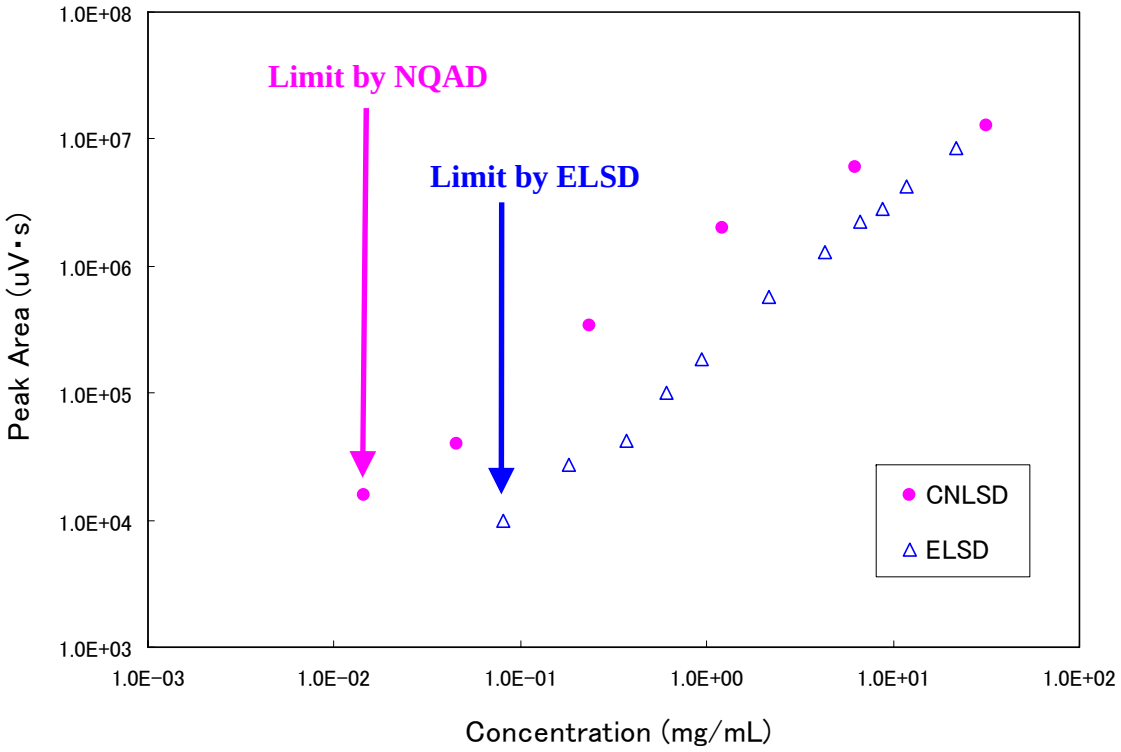

Figure 4 Concentration dependence of CNLSD and ELSD for the PEG oligomer solutions with the degree of polymerization index *n* = 18.

Comparison to the Certified Value and the ELSD Result

- **Peak areas by CNLSD is much closer to the certified value of PEG 1000 than those by ELSD.**

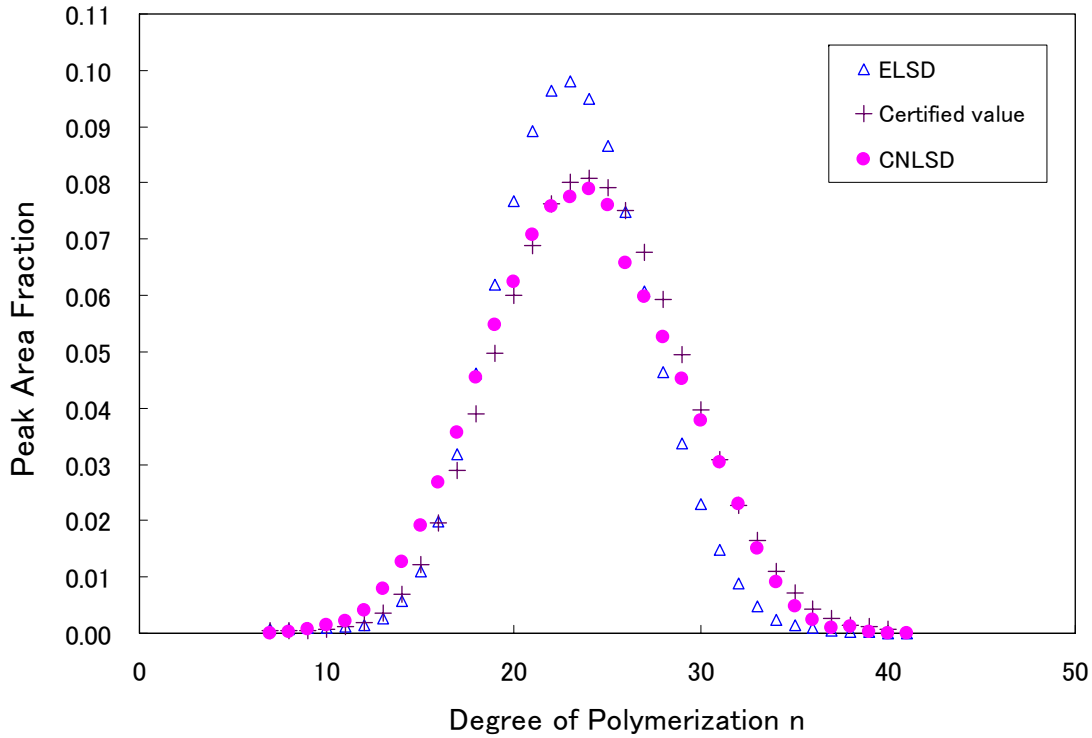

Figure 5 SFC chromatograms of PEG 1000 by CNLSD and by ELSD compared to the certified values.

Conclusions

- **We checked the performance of CNLSD which was connected to SFC by using certified reference material PEG 1000 (NMIJ CRM 5006a) produced in our laboratory.**
- **Sensitivity and repeatability of the CNLSD is high enough compared to those of ELSD. The limit of detectable concentration for PEG 1000 by CNLSD is 10 times lower than that by ELSD.**
- **Compared to ELSD, the quantitativeness of CNLSD is so good that the molecular mass distribution of PEG 1000 can be closely determined without any calibrations of detections.**