Abstract

Novel colorimetric formaldehyde-sensing molecules (**KD-XA01** and **KD-XA02**) possessing an enaminone structure were designed and synthesized. These sensing molecules produced a red shift from 350 nm to 425 nm in the absorption spectra after the reaction with formaldehyde and its color changes from colorless to yellow, which was caused by the fact that the enaminone structure in the reagent reacts with formaldehyde to give the lutidine derivative in solution or solid phase. This color change prevented a background signal and guaranteed highly sensitive and selective detection of formaldehyde. As an application of these reagents, a handy and rapid monitoring system has been developed for detecting HCHO gas in air using a highly sensitive and selective porous cellulose paper that contains a silica gel as an absorbent and impregnated with a processing solution which was constructed from a novel colorimetric reagent (**KD-XA01**), and phosphate buffer in MeOH under optimum conditions. This monitoring method is based on a color change on the surface of the paper, which was caused by the fact that the enaminone structure of **KD-XA01** reacts with formaldehyde to give the lutidine derivative. When the detection tablet was exposed to air containing formaldehyde, the surface color of the tablet changed from white to yellow and the degree of the color change was monitored as the function of the intensity of the reflected light illuminated by an LED (475 nm). The degree of the response was proportional to the HCHO concentration at a constant sampling time and flow rate and, 0.05 ppm HCHO which is under the standard value set by WHO was able to be detected at 5 min. The detection limit was 0.005 ppm. Moreover, this monitoring system was not interfered by carbonyl compounds such as acetaldehyde and acetone, alcohols, other hydrocarbons and typical gases such as carbon monoxide, carbon dioxide, nitrogen dioxide, etc. It was possible to monitor the HCHO gas in a room using this instrument and the response values were in good agreement with those obtained by DNPH method. This highly sensitive and selective HCHO gas monitor using **KD-XA01** is widely applicable as a convenient method.

Properties of Formaldehyde (HCHO)

- Highly Lachrymatory, Odorous, and Physiologically Active Substance
- Typical Toxic Gases
- Injury of the Eyes, Noes and Respiratory Organ
- Cause of the Allergies

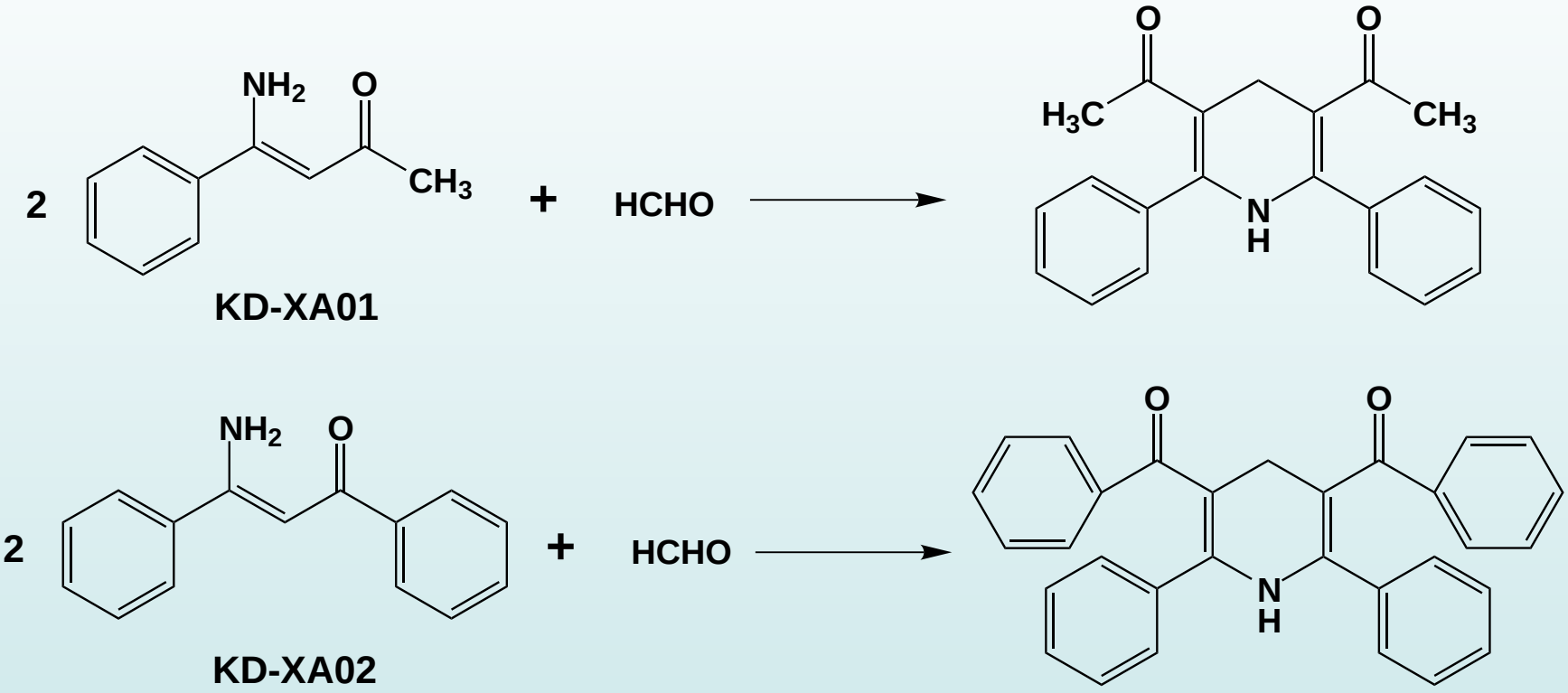
WHO has set a standard of 0.08ppm in air averaged over 30 min.

The Method of the Conventional HCHO Detection

- Detector Tube
- Passive Sampling
- DNPH Method
- Chemical Luminescence
- Active Sampling
- GC / MS

- Expensive analytical instruments and sensitive technique are needed.
- It takes a long time to obtain the results.
- The analytical reagents are toxic.
- Foreign substances interfere with the correct HCHO measurement.

Chemical Structures of KD-XA01 and KD-XA02



- **Smooth and mild reaction condition**
- **Reduced interference from foreign substance**
  →High Selectivity to HCHO
- **Higher Molar Extinction Coefficient**
- **Change of Colorless Reactant to the Colored Product**

Experimental Conditions

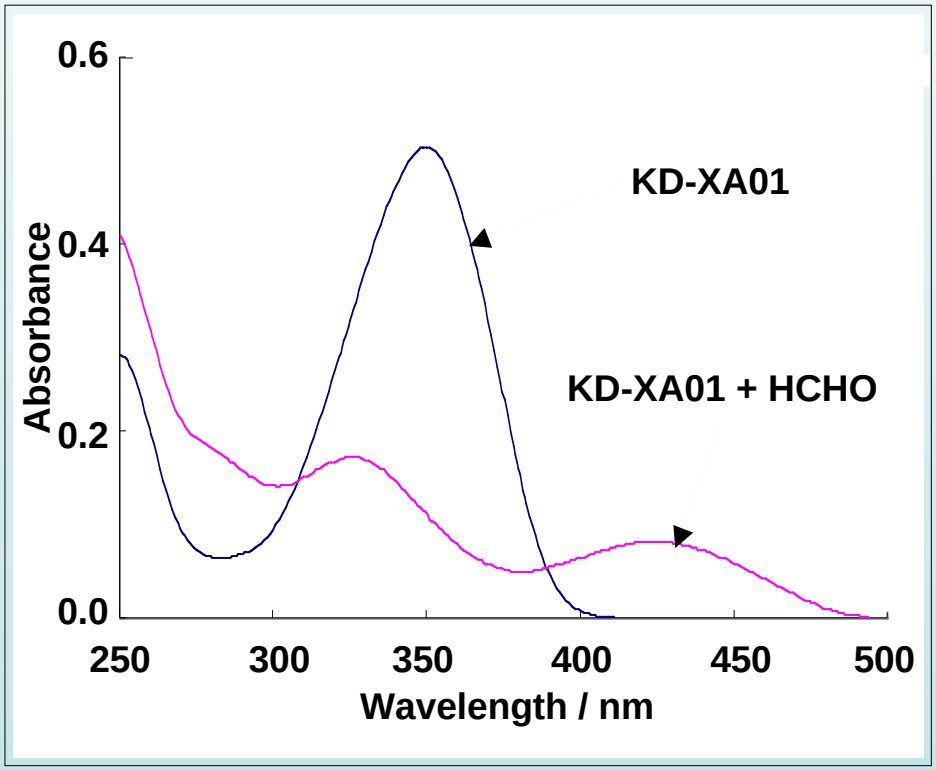
- **Concentration ; [KD-XA01] = [KD-XA02] = 20.0 μM**
  [HCHO] = 0 ~ 10.0 μM

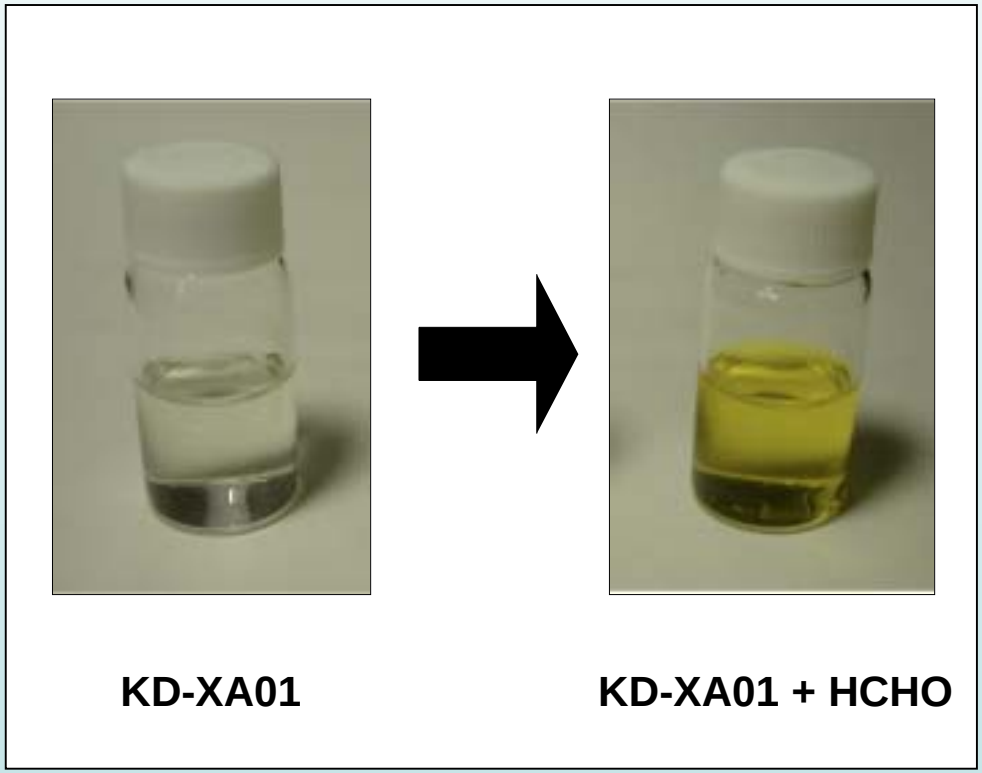
- **Solvent ; Acetonitrile : Phosphate Buffer = 2 : 1 v/v**

- **Reaction Temperature ; Room Temperature**

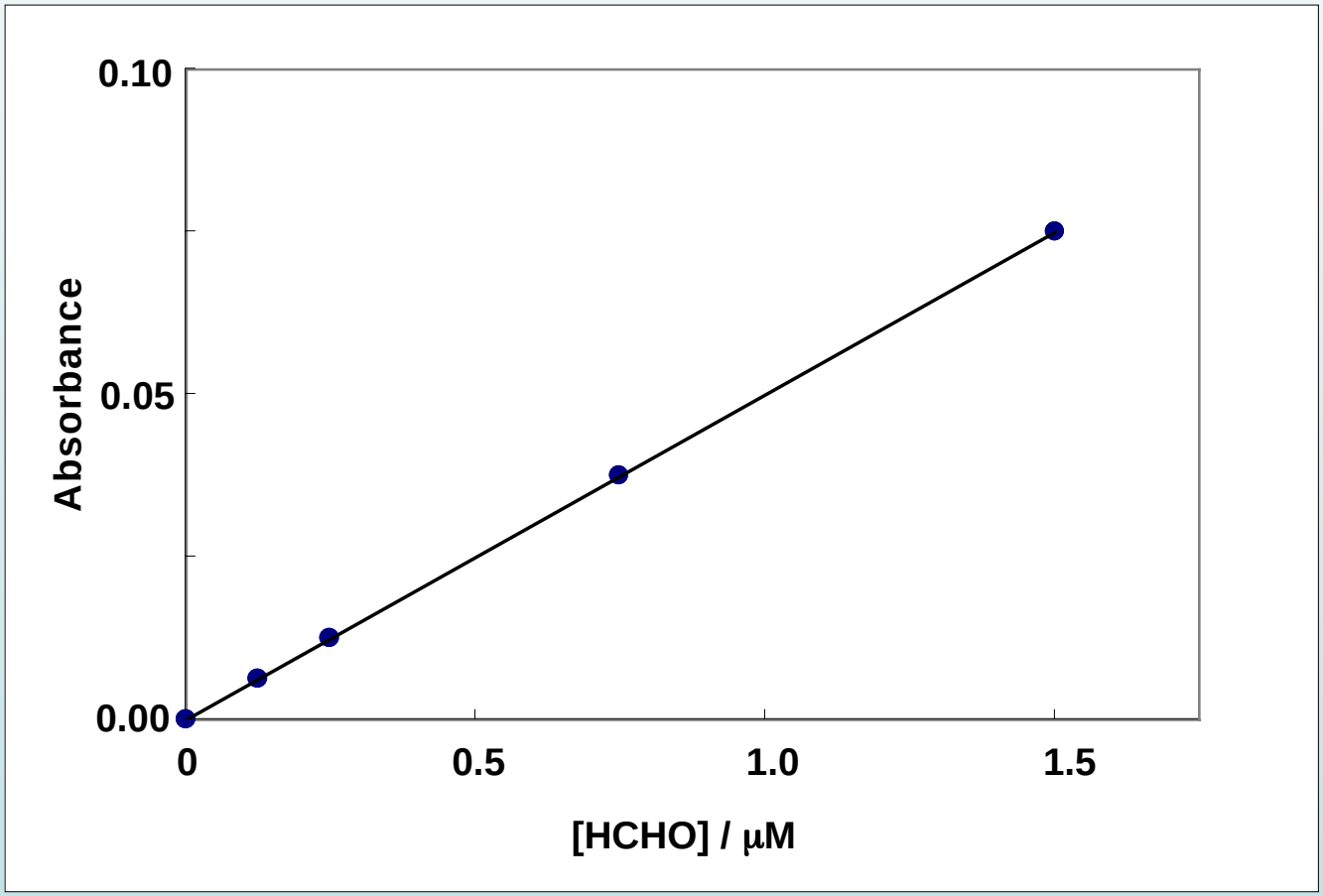
- **Procedure ; A mixture of HCHO and KD-XA01 or KD-XA02 in a screw-capped vial was stirred. After the reaction the solution was measured by absorption spectrometer.**

Absorption Spectra of KD-XA01 before and after the Reaction with HCHO and the Color Change of the Solutions

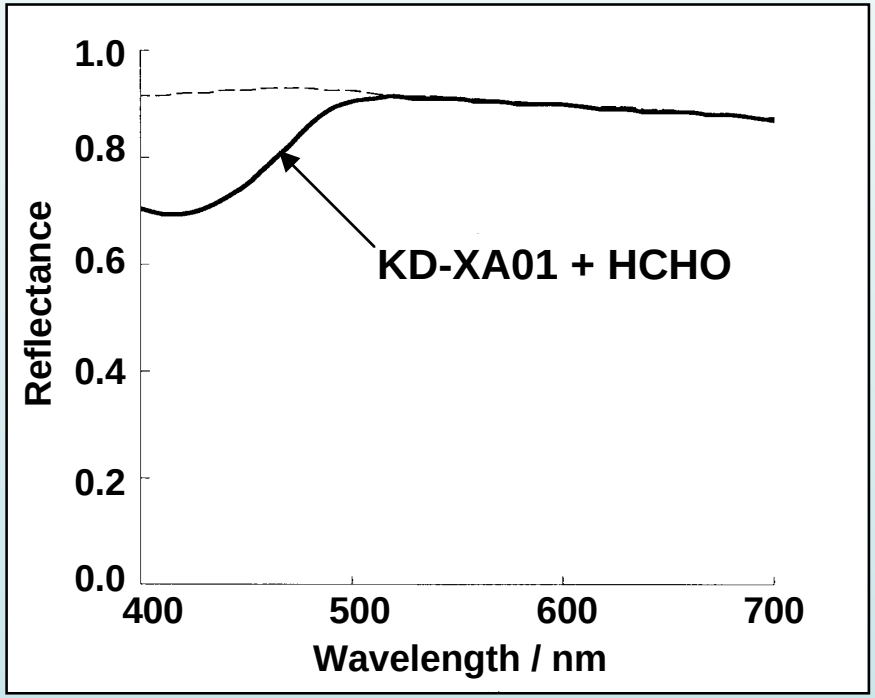


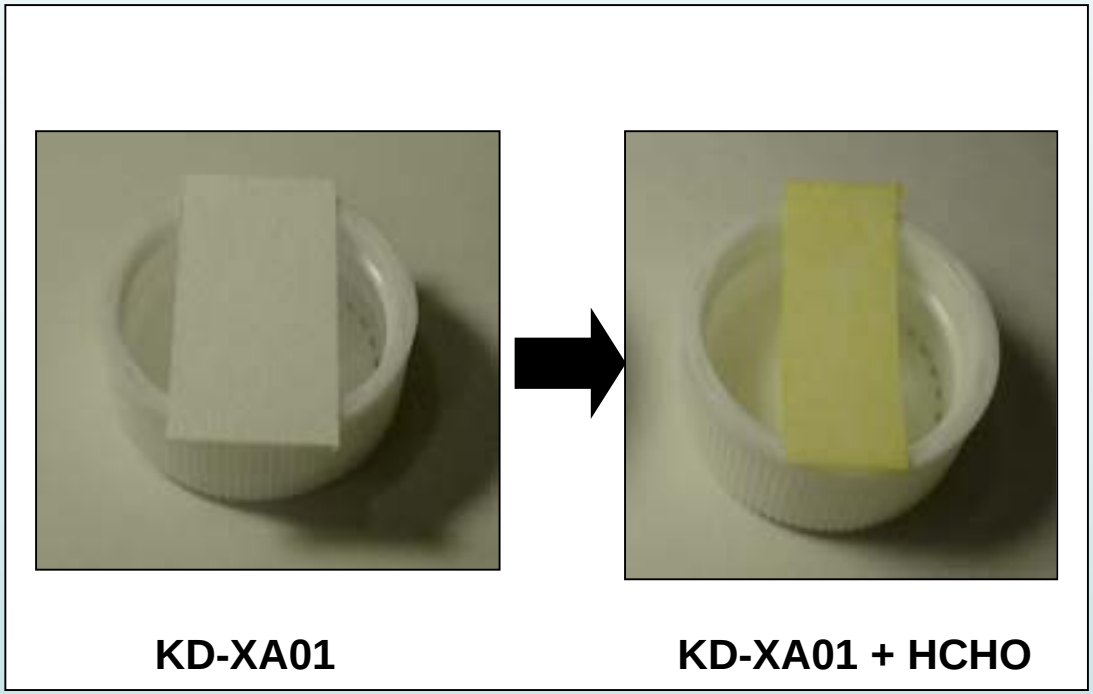


The Plot of the Absorbance at 420 nm as a Function of HCHO Concentration

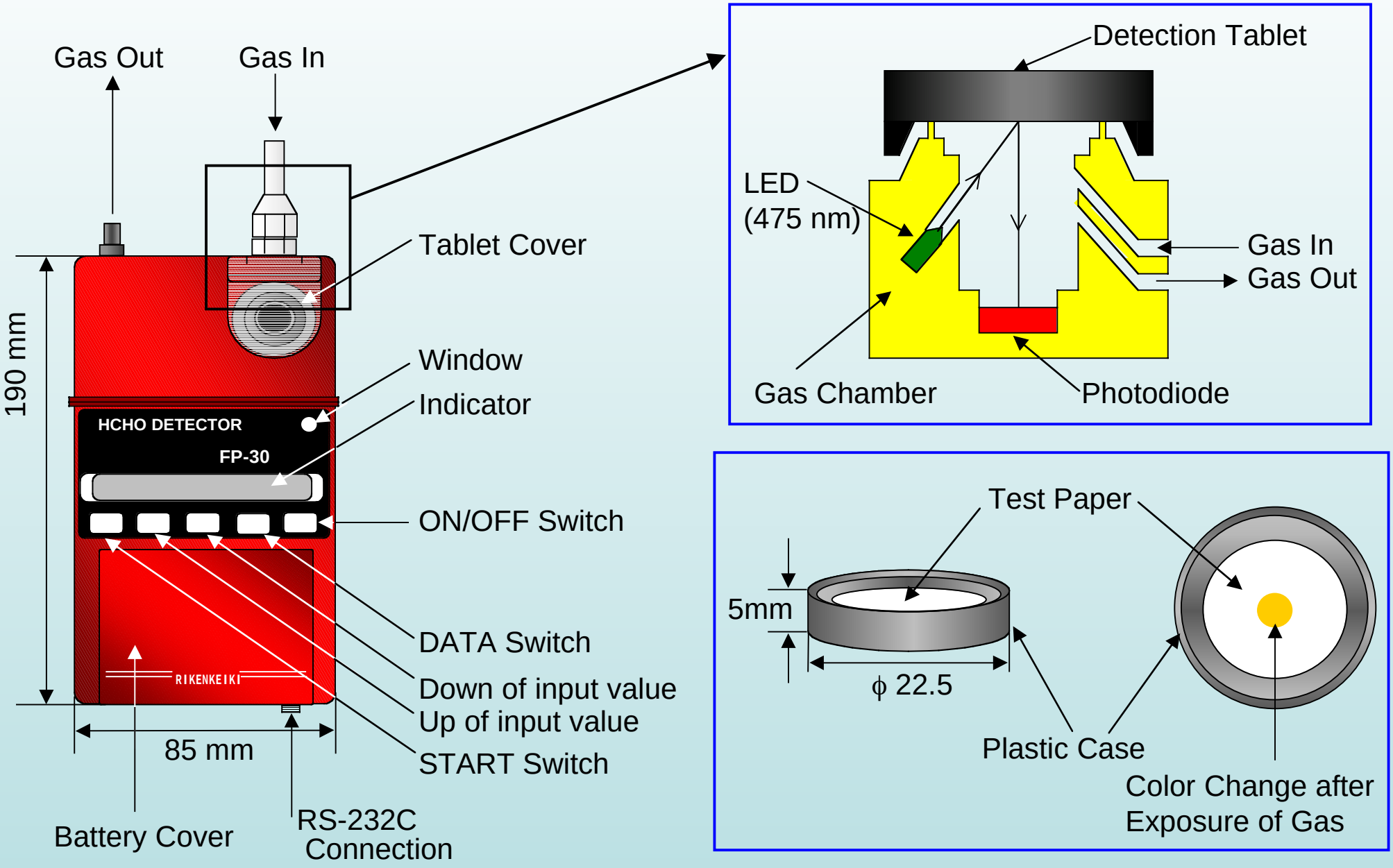


Reflectance Spectra of KD-XA01 before and after Reaction with HCHO Gas and the Color Change of the Filter Paper Containing KD-XA01





HCHO Monitoring Instrument (FP-30)



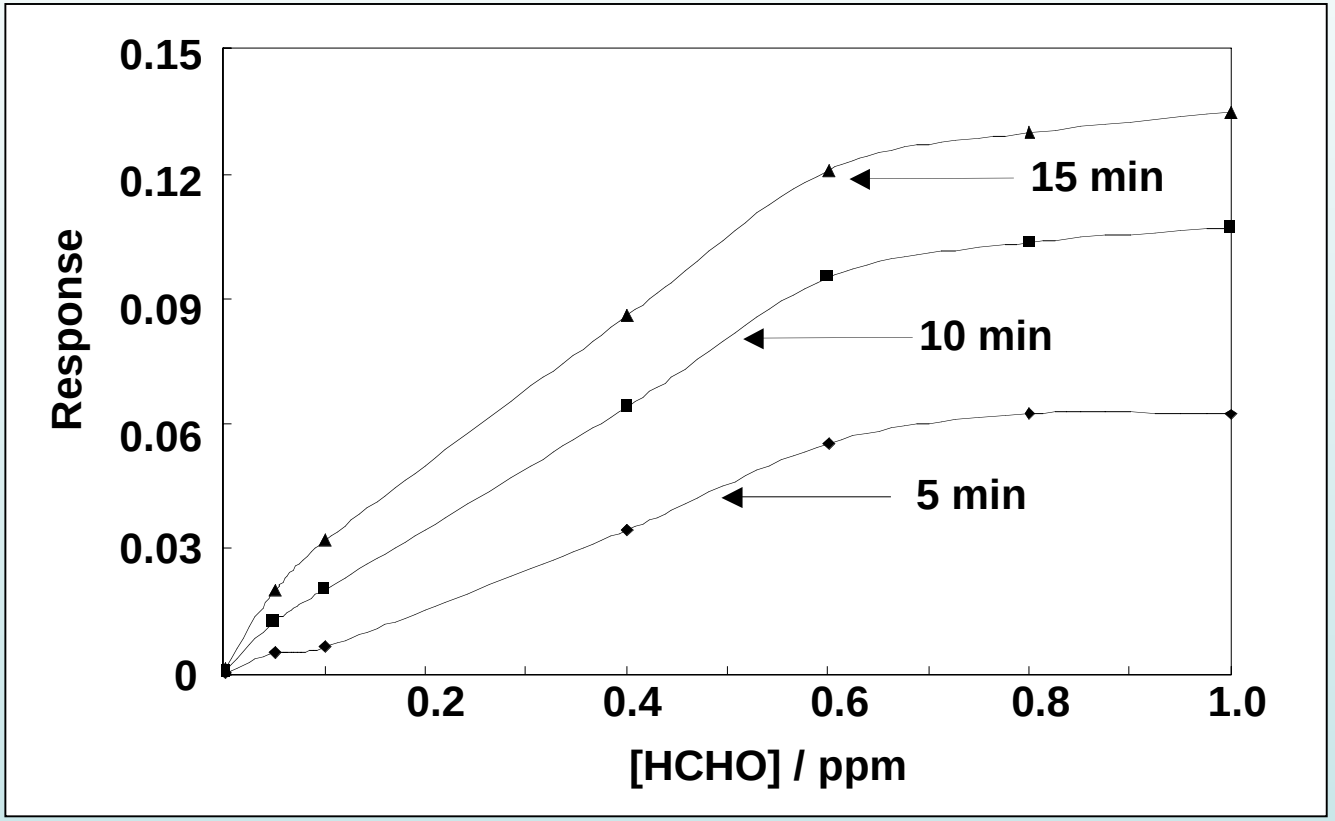
Experimental Conditions

- Preparation of the Detection Tablet : **KD-XA01** was dissolved at a concentration of 0 ~ 1.0 wt% in MeOH : phosphate buffer = 9 : 1v/v. The paper was impregnated with this processing solution for 1 min and then dried in an oven for 1 min at 55 °C. This paper was fixed in a plastic case and stored in an aluminium bag in vacuo.

- Apparatus : The degree of the color change was recorded by measuring the relative reflectance at 475 nm. The output voltage of the photodiode is proportional to the intensity of the reflected light, and the degree of the color change is calculated according to the following equation: Response = $-\log(V_1/V_0)$, where V_0 and V_1 are outputs of a blank (atmospheric air) and of the sample gas, respectively.

- Flow rate of the gas : 250 ml / min

Relationship between the Response and HCHO Concentration at Various Sampling Times (5min, 10min, 15min)



- It was possible to detect 0.05 ppm HCHO gas, which is under the standard value set by WHO, for 5 min as a minimum time.
- The detection limit was 0.005 ppm

Selectivity of HCHO against Foreign Gases

Gas	Concentration	Response (ppm)	Gas	Concentration	Response (ppm)
Toluene	1 %	0	Carbon Dioxide	1%	0
Xylene	1 %	0	Hydrogen	100%	0
Ethylbenzene	8800ppm	0	Acetic Acid	20ppm	0
Stylene	1000ppm	0	Hydrogen Sulfide	30ppm	0
Di-*n*-butyl Phthalate	80ppm	0	Hydrogen Fluoride	6ppm	0
Acetaldehyde	100ppm	0	Hydrogen Chloride	1ppm	0
Propionaldehyde	100ppm	0	Chlorine	3ppm	0
Ethanol	1%	0	Acetone	1%	0
Ethyl Acetate	1000ppm	0	1-Butanol	7000ppm	0
Carbon Monoxide	100ppm	0	Methyl Ethyl Ketone	1000ppm	0
Nitrogen Monoxide	100ppm	0	Benzene	1%	0
Nitrogen Dioxide	10ppm	0	Formaldehyde + NH_3	0.1 ppm + 10 ppm	0.1
Sulfur Dioxide	15ppm	0	Formaldehyde	0.1 ppm	0.1

Comparison of This Method with Other Monitoring System

	TAB (KD-XA01)	TAB (HA)	Detection Tube
Ammonia	○	×	△
Nitrogen Dioxide	○	○	△
Hydrogen Chloride	○	×	△
Acetone	○	×	×
Acetaldehyde	○	×	×

○ : without interference, △ : removal of low concentration gas after the pre-treatment
× : with interference

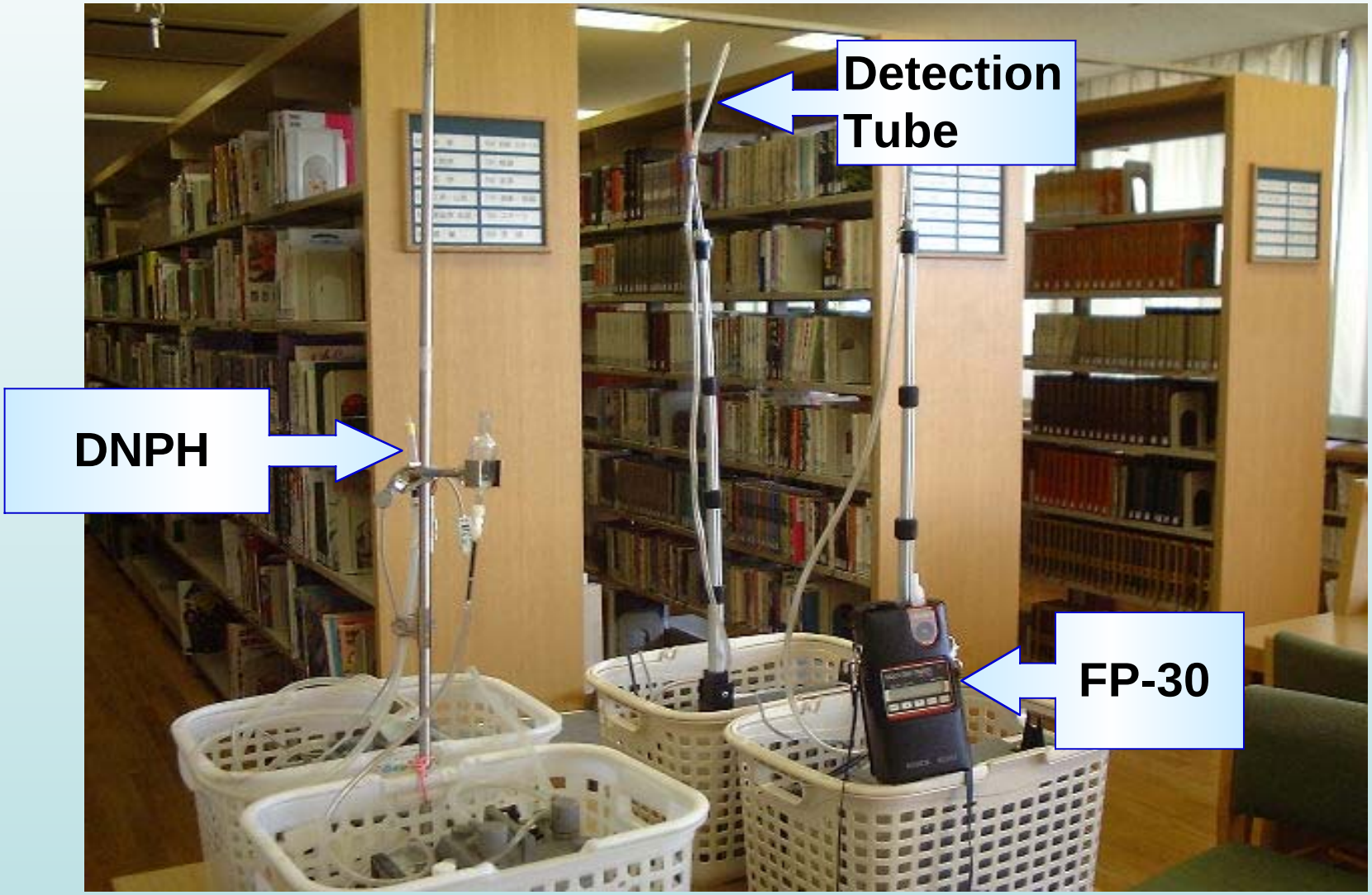
Detection of HCHO in the Room of the New Apartment

Detection of HCHO Gas in the Room

Detecting Place	This Method (ppm)	DNPH (ppm)
Closet	0.030	0.03
Living Room	0.020	0.02
Furniture	0.040	0.05

The concentration of HCHO using this method was in good agreement with that of the DNPH method

Detection of HCHO in the Room of the School



Detection of HCHO in the Rooms of the Various Schools

	FP-30 (ppm)	DNPH (ppm)	Temperature (°C)	Humidity (%RH)
School A	0.025	0.024	22.9	41
	0.025	0.026	22.6	40
	0.050	0.041	22.5	25
	0.025	0.018	22.7	38
School B	0.000	0.001	17.7	31
	0.010	0.009	17.9	38
	0.025	0.023	18.5	50
	0.010	0.008	18.3	33
School C	0.015	0.019	18.4	50
	0.015	0.019	18.4	50
	0.010	0.008	18.3	33
	0.010	0.007	17.5	27

Conclusions

・Designed and synthesized two novel analytical reagents, **KD-XA01** and **KD-XA02** were successfully applied for the highly selective and highly sensitive detection of HCHO by monitoring the color change.

・These reagents have a high selectivity for HCHO; while other gases such as acetaldehyde, toluene and benzene did not interfere with the monitoring of HCHO.

・As an application of these reagents, the highly selective and highly sensitive detection of HCHO gas was performed using portable HCHO monitoring instrument composed by a detection tablet which is impregnated with **KD-XA01**.

・The successful demonstration of the detection of HCHO gas in the range of 0.05 ～ 1.0 ppm in a short time was performed using a gas detector containing a detection tablet (0.05 ppm HCHO was able to be detected at 5 min as a minimum time).

・The HCHO gas in the environment was able to be monitored and was in the good agreement with the DNPH method.