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Proposal of AAA-battery-size one-shot ATR Fourier spectroscopic imager for on-site analysis - Simultaneous measurement of multi-components with high accuracy –

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ABSTRACT

For simultaneous measurement of multi-components on-site like factories, the ultra-compact (diameter: 9[mm], length: 45[mm], weight: 200[g]) one-shot ATR (Attenuated Total Reflection) Fourier spectroscopic imager was proposed. Because the proposed one-shot Fourier spectroscopic imaging is based on spatial-phase-shift interferometer, interferograms could be obtained with simple optical configurations. We introduced the transmission-type relative-inclined phase-shifter, that was constructed with a cuboid prism and a wedge prism, onto the optical Fourier transform plane of infinity corrected optical systems. And also, small light-sources and cameras in the mid-infrared light region, whose size are several millimeter on a side, are essential components for the ultra-compact spectroscopic configuration. We selected the Graphite light source (light source area: 1.7×1.7[mm], maker: Hawkeye technologies) whose radiation factor was high. Fortunately, in these days we could apply the cost-effective 2-dimensional light receiving device for smartphone (e.g. product name: LEPTON, maker: FLIR, price: around 400USD). In the case of alcoholic drinks factory, conventionally workers measure glucose and ethanol concentrations by bringing liquid solution back to laboratories every day. The high portable spectroscopy will make it possible to measure multi-components simultaneously on manufacturing scene. But we found experimentally that absorption spectrum of glucose and water and ethanol were overlapped each other in near infrared light region. But for mid-infrared light region, we could distinguish specific absorption peaks of glucose (@10.5[μm]) and ethanol (@11.5[μm]) independently from water absorption. We obtained standard curve between absorption (@9.6[μm]) and ethanol concentration with high correlation coefficient 0.98 successfully by ATR imaging-type 2-dimensional Fourier spectroscopy (wavelength resolution: 0.057[μm]) with the graphite light source (maker: Hawkeye technologies, type: IR-75).

Keywords: Quantitative measurement, Fourier spectroscopy, Mid-infrared light, Portable spectroscopic apparatus, Glucose, Ethanol, Spatial phase shift interferometer systems

1. INTRODUCTION

Because conventional FTIR (Fourier Transform Infrared spectroscopy) equipped with ATR (Attenuated Total Reflection) is expensive and large-size apparatus, on-site measurements of foods or drinks on manufacturing scene are impractical. Because the proposed one-shot Fourier spectroscopic imager is a kind of spatial-phase-shift interferometer, the phase-shifter could be simply configured with a cuboid prism and a wedge prism without mechanical movements. Because of near common path interferometer, our proposed method has the strong robustness against mechanical vibrations that is applicable for unstructured environments. And the beans-size apparatus that could be introduced into smartphones will be realized, because only the transmission-type relative-inclined phase shifter is installed into infinity corrected optical systems. Therefore, because our proposed method could be applied for in-situ monitoring inside of the manufacturing factory or equipment, daily quality control could be realized for alcoholic drinks such as alcohol(=Ethanol) and glucose concentration.

Generally speaking, from the quantitative-analysis point of view, mid-infrared spectroscopy is superior to near-infrared one. Bur for avoiding water absorption in mid-infrared light region, thin liquid-cells whose thickness are several micro

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meter should be used. In this case, filling solution into thin liquid cells or cleaning cells will be time-consuming jobs. Thus, we determined to introduce ATR into our proposed method, because only dropping solutions on ATR prism will be sufficient for measurement without difficulties.

In chapter 2, the conceptual optical configuration of AAA-battery-size one-shot ATR Fourier spectroscopic imager is mentioned. In chapter 3, with comparing with near-infrared spectroscopy, we verified that mid-infrared spectroscopy absorption would be suitable for independent component analysis for alcoholic drinks. At chapter 4, we discuss merits of mid-infrared spectral absorption for independent component analysis of glucose and ethanol with liquid cells. And we obtained standard curve between absorption (@9.6[μm]) and ethanol concentration with high correlation coefficient 0.98 successfully by ATR imaging-type 2-dimensional Fourier spectroscopy.

2. AAA-BATTERY-SIZE ONE-SHOT ATR FOURIER SPECTROSCOPIC IMAGER

As shown in figure 1, the proposed one-shot Fourier spectroscopic imaging[1]-[3] is a kind of spatial phase shift interferometer that has the transimission-type relative-inclined phase-shifter onto optical Fourier transform plane of infinity corrrected optical systems. Relative-incline phase-shifter consists of a wedge and cuboid glass for giving spacial phase-shifts at half-flux of objective beams. Therefore, the transmitted beams through each prism intersect from oblique angle and form spatial fringe patterns as interferograms on a imaging plane [1]-[3]. If the transmission-type relative-inclined phase-shifter could be made by a thin glass plate such as a cover glass whose thickness is around 0.3[mm], we can realized the bean-size spectroscopic imager that will be mounted on smartphones [4]. Conventional wavelength dispersive spectrometers need long optical path length to secure wavelength resolution. On the contrary, because small inclination angle is sufficient for forming of interferograms, our proposed method needs only very short optical path length. For configuring ultra-compact spectroscopy, we selected the Graphite light source (light source area: 1.7×1.7 [mm],canned external dimensions: 2.2×2.2 [mm], maker: Hawkeye Technologies, output power: 767tipical / 1000Max [mm]). In recent years, cost-effective and ultra-compact 2-dimentional light receiving device, whose diameter is around one dime (maker: FLIR, type: FLIR-ONE, price: around 400USD), became to be commercially available products. In this paper, we also proposed to introduce ATR method into our extremely compact one-shot Fourier spectroscopic imaging for appling mid-infrared spectroscopy.

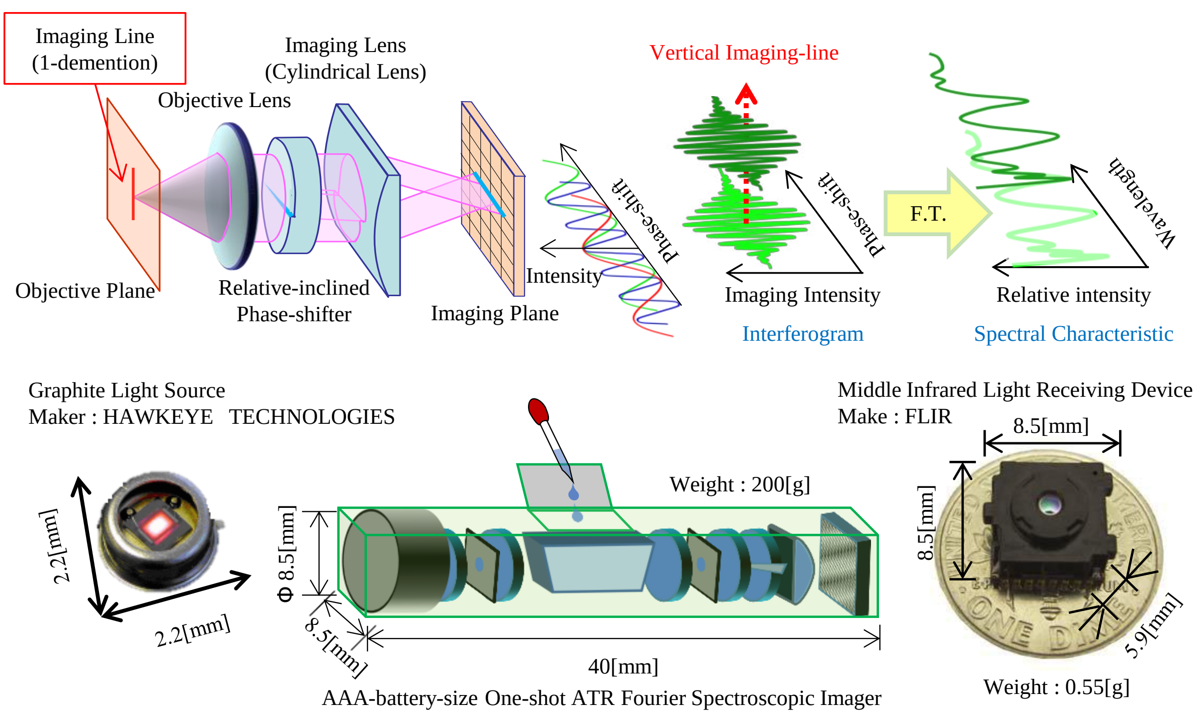


Fig.1 Configuration of AAA-battery-size ATR Fourier spectroscopic apparatus based on one-shot Fourier spectroscopic imager.

3. ISUUES OF NEAR-INFRARED LIGHT ABSORPTION FOR INDEPENDENT COMPONENT ANALYSIS OF GLUCOSE AND ETHANOL

3.1 Verification of bad influences on spectral-absorbance standard curve of glucose affected by ethanol concentration differences measured by the proposed one-shot Fourier spectroscopy

We verified the difficulties of independent component analysis for glucose and ethanol in near-infrared region. We had already reported the measurement accuracy of glucose solution with the one-shot Fourier spectroscopy that satisfied the target accuracy 10[mg/dl] in liquid cells [3]. But as shown in figure 2(b), for mixed solution of multiple components, we verified that cross-interactions of overlapped spectrum were unavoidable problems in near-infrared light region.

The standard curve, that is shown in Fig.2 (b), was acquired by our proposed one-shot Fourier spectroscopy (wavelength range: 900-1200[nm], wavelength resolution: 37.7[nm]). To verify cross-interaction between glucose and ethanol, we keep the glucose concentration and change the ethanol concentration only to make mixed solution. In this case, the constant absorbance of glucose concentration at wavelength 1579[nm] will be expected to stabile independent with changing of ethanol concentration.

We prepared mixed solutions with same glucose concentration (1.0×10^4 [mg/dl]) and different ethanol concentrations (10, 20, 30[ml/dl]). The one-shot Fourier spectroscopy can measure within one frame image with high time resolution. For statistical improvement of light-source fluctuation (maker: FIANIUM, type: Supercontinuum Fiber Laser400-4), the averaged 3600 data（60 frame images × 60 [s]） were plotted onto the standard curve as shown in Fig.2 (b). Unfortunately, absorption at peak value of glucose (@1579[nm]), that was expected to keep constant value, were varied in accordance with changing of ethanol concentrations. Unexpected cross-interaction of glucose absorbance was changed from 0.438 to 0.367 that was corresponds to 5×10^3[mg/dl] as I discuss later in section 3.2. Thus, even if glucose concentration was not changed, estimated concentration from absorbance was miscalculated. Therefore, we verified difficulties of the independent component analysis for glucose and ethanol mixed-solution in near-infrared light region. In the next section 3.2, we demonstrated issues that glucose absorption (@1579[nm]) was on the shoulder of absorption curve of water absorbance (@1400[nm]) and ethanol (wavelength @1700[nm]).

3.2 Verification of cross-interaction for glucose absorption peak (@1579[nm]) on the shoulder of absorption curve of water (@1400[nm]) and ethanol (wavelength @1700[nm]) by conventional wavelength dispersive spectrometers

As shown in Fig.2 (a), using the conventional wavelength dispersive spectrometer (maker: Shimadzu Co., type: Solid Spec-3700), we verified cross interactions for glucose absorption peak (@1579[nm]) that was on the shoulder of absorption curve of water (@1400[nm]) and ethanol (wavelength @1700[nm]).

We estimated that the cross-interaction will be problems or not. First, we made mixed solutions as same as previously explained in section 3.1. We keep the constant glucose concentration (1.0×10^4 [mg/dl]) and changed ethanol concentrations (0, 10, 20, 30 [ml/dl]). As shown in Fig.2 (b), because the cross-interaction glucose absorption change 0.04 was corresponds to glucose concentration change 5×10^3[mg/dl]. The cross-interaction error 5×10^3[mg/dl] is 50 times of target accuracy 100[mg/dl]. As shown in upper side of Fig.2 (b), the glucose absorption (@1579[nm]) was on the shoulder of absorption curve of water (@1400[nm]) and ethanol (@1700[nm]). Thus, with increasing of amount of ethanol concentration, the amount of water was relatively decreasing, as illustrated in lower side of Fig.2 (a). Thus, we thought that water absorbance (@1400[nm]) was relatively decreasing. On the contrary, ethanol absorption (@1700[nm]) was increasing. Thus, like seesaw as illustrated in lower side of Fig.2 (a), glucose absorption (@1579[nm]) on both shoulder was changed (changed absorbance: 0.04) even if glucose concentration was constant.

We determined near-infrared spectroscopy was not suitable for independent component analysis of glucose and ethanol. Thus, in next chapter, we evaluated the effectiveness of mid-infrared spectroscopy for independent component analysis with liquid cells and one-shot ATR Fourier spectroscopy.

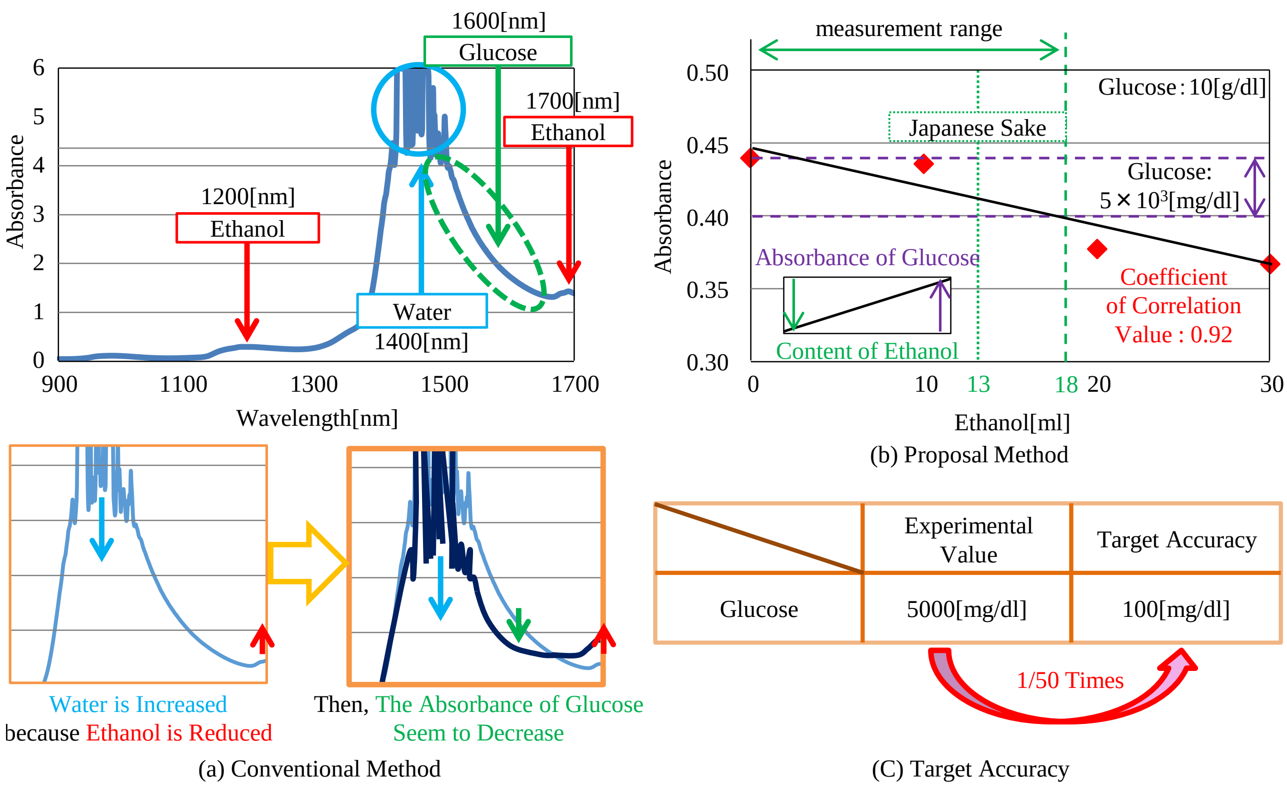


Fig.2 Measurement data of the Glucose solution and Ethanol concentration in the near-infrared region.

4. EFFECTIVENESS EVALUATION OF MID-INFARED SPECTROSCOPIC ABOSORPTION FOR INDEPENDENT CONPONENT ANALYSIS

4.1 Examination of the possibility of independent component analysis using high-sensitive imaging-type 2-dimensional Fourier spectroscopy with liquid cells

First, paying attention on high sensitivity, to evaluate the effectiveness of mid-infrared absorption, we used the proposed imaging-type 2-dimensional Fourier spectroscopy with liquid cells [1] [4] [5]. One-shot Fourier spectroscopy is based on the imaging-type 2-dimensional Fourier spectroscopy to improving the time resolution. For sensitivity, imaging-type 2-dimensional spectroscopy is superior to one-shot type.

Solution (ethanol: 96[%]) in thin liquid cell (thickness: 12[μm]) was measured by the imaging-type 2-dimentional Fourier spectroscopy (light source: blackbody, temperature: 120[℃]). As shown in figure 3, we could identify ethanol absorption at 9.3 [μm], 9.6 [μm] and 11.5[μm]. And also we could distinguish glucose absorption at 10 [μm] respectively. We could evaluate the effectiveness of independent component analysis for ethanol and glucose by mid-infrared absorption with thin liquid cells.

Furthermore, we obtained standard curve of ethanol concentration (0-30[ml/dl]) and relative absorbance difference (background correction: ethanol absorbance @11.5[μm] - glucose absorbance @10[μm]) in conditions of constant glucose concentration (5×10^3 [mg/dl]). As shown in figure 4, we successfully got high correlation coefficient 0.96.

But using thin liquid cells on-site will be time consuming jobs as mentioned before. Thus, in next section 4.2, we demonstrated the feasibility of ATR method by the imaging-type 2-dimensional Fourier spectroscopy.

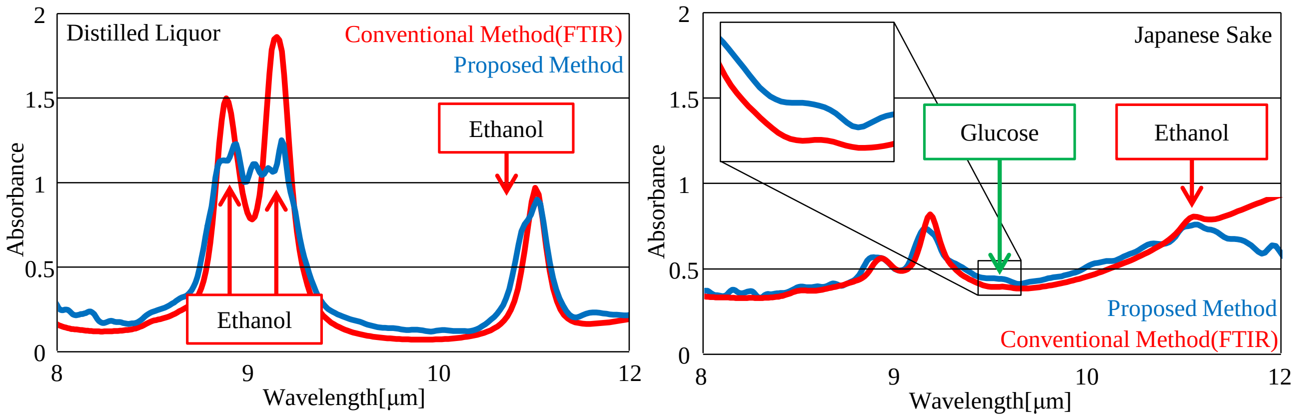
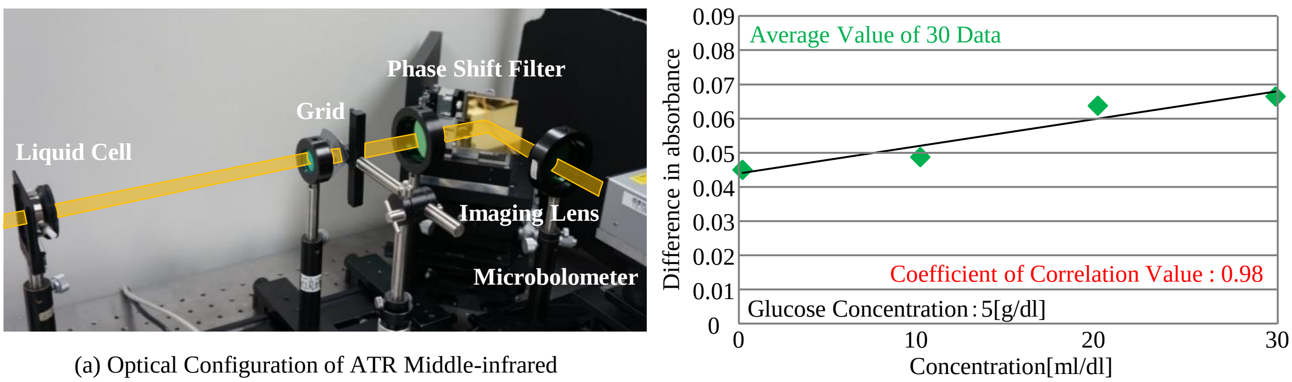


Fig.3 Spectral absorbance of ethanol and glucose, Distilled liquor and Japanese sake.



(a) Optical Configuration of ATR Middle-infrared 2-dimensional Fourier-spectroscopy

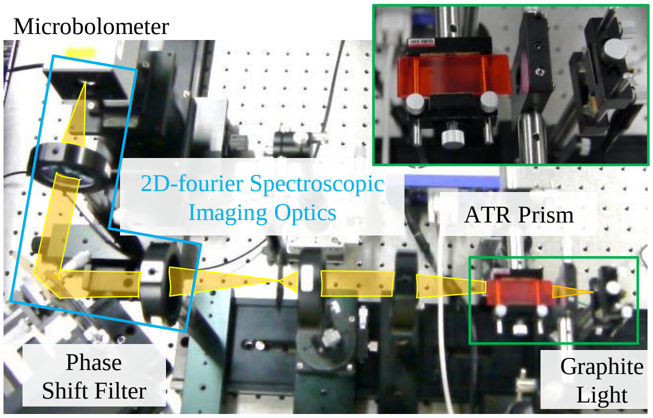
(b) Quantitative Measurement of Ethanol

Fig.4 Imaging-type 2-dimensional Fourier spectroscopy optical system and Graph of measurement results.

4.2 Quantitative ethanol measurement by ATR imaging-type 2-dimensional Fourier spectroscopy

As shown in figure 5 (a), we evaluated the quantitative ethanol measurement by ATR imaging-type 2-dimensional Fourier spectroscopy (phase-shift stroke: 1500[μm], sampling interval: 1417[nm], wavelength resolution: 0.057[μm]) with the graphite light source (maker: Hawkeye Technologies, type: IR-75). We used 2 types ATR prism that was trapezoidal (material: KRS-5, size: 50×20×2[mm], incident angle: 60 [deg.]) and right triangle (material: ZnSe, size: 18×18×18[mm]). We could recognize ethanol (concentration: 99.5%) absorption(@ near 9[μm], 10.5[μm] and 11.5[μm]) by trapezoidal prism (four-times internal-reflection type).

Also right triangle prism (one-time internal-reflection type) detected ethanol absorption at same wavelength with 4 kinds of solution (concentration: 20-100[%]). As shown in Fig.5 (b), we obtained standard curve between absorption (@9.6[μm]) and ethanol concentration with high correlation coefficient 0.98 successfully.



(a) Optical Configuration of ATR Middle-infrared
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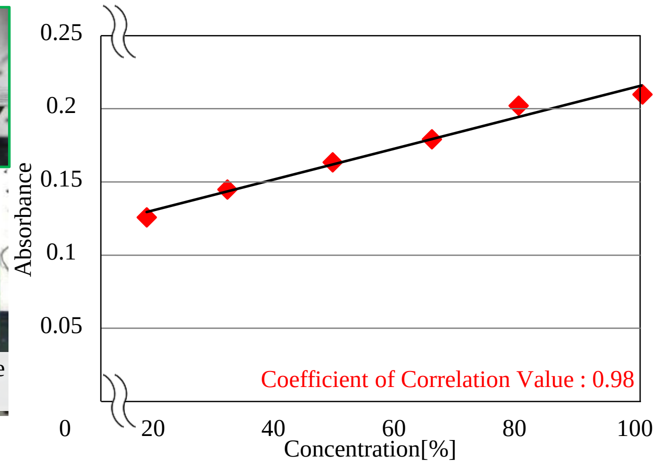

(b) Quantitative Measurement of Ethanol

Fig.5 Imaging-type 2-dimensional Fourier spectroscopy optical system
and Graph of measurement results of Ethanol.

5. CONCLUSION

For simultaneous measurement of multi-components on-site like factories, the ultra-compact (diameter: 8.5[mm], length: 45[mm], weight: 200[g]) one-shot ATR (Attenuated Total Reflection) Fourier spectroscopic imager was proposed. But we found experimentally that absorption spectrum of glucose and water and ethanol were overlapped each other in near infrared light region. Thus, the independent component analysis of alcoholic drinks became to be difficult problems. But for mid-infrared light region, we could distinguish specific absorption peaks of glucose (@10.5[μm]) and ethanol (@11.5[μm]) independently from water absorption. We obtained standard curve between absorption (@9.6[μm]) and ethanol concentration with high correlation coefficient 0.98 successfully by ATR imaging-type 2-dimensional Fourier spectroscopy (phase shift stroke: 1500[μm], sampling interval: 1417[nm], wavelength resolution: 0.057[μm]) with the graphite light source (maker: HAWKEYE TECHNOLOGIES, type: IR-75).

In future works, we will obtain glucose concentration standard curve and evaluate independent component analysis with one-shot ATR Fourier spectroscopic imager.

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