Development of Portable Gas Chromatograph Using Ball Surface Acoustic Wave Sensor with Air Carrier Gas for Crewed Space Environment Monitoring

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In a crewed space environment, monitoring of trace volatile organic compounds in the atmosphere is necessary to ensure the health of the crews and the vehicle systems. Gas chromatographs (GC) are one of the effective tools for analyzing such a wide variety of gases. We have developed a prototype of 1 L sized GC using a ball surface acoustic wave (SAW) sensor, a small and high sensitivity sensor that utilizes multiple roundtrips of the SAW on a spherical element, as the GC's detector. However, the prototype used a hydrogen storage canister to supply the carrier gas, which required strict safety measures for use in space. On the other hand, using supplying nitrogen or helium, which are safe gases, with high-pressure cylinders would increase the weight of the GC system. Therefore, we are studying using recirculated air as a carrier gas without cylinders. However, using air as carrier gas results in lower separation performance than using hydrogen. In this study, we developed a portable GC using the ball SAW sensor with air carrier gas and demonstrated the feasibility of acceptable separation performance.

Nomenclature

BS	=	ball SAW sensor	*PDMS*	=	poly-dimethylsiloxane
CL	=	column	*PF*	=	purifier
CP	=	circulation pump	*PNVP*	=	poly-N-vinylpyrrolidone
DTC	=	delay time change	*PR*	=	pressure regrater
FID	=	flame ionization detector	*SAW*	=	surface acoustic wave
GC	=	gas chromatograph	*SP*	=	sample pump
IDT	=	interdigital transducer	*TCR*	=	temperature coefficient ratio
ISS	=	international space station	*VOC*	=	volatile organic compound
PC	=	pre-concentrator	f_1 and f_2	=	frequencies
A_1 and A_2	=	temperature coefficients at f_1 and f_2	w	=	gas concentration
$B(T)$	=	sensitivity factor	$G(w)$	=	function of gas concentration w

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τ_1 and τ_2 = delay times of SAW at f_1 and f_2
T = sensor temperature
C = temperature coefficient ratio (TCR)
Δt_W = DTC depend on gas concentration
$\Delta\tau_1$ and $\Delta\tau_2$ = DTCs of SAW at f_1 and f_2
T_{REF} = reference temperature
Δt_T = DTC depend on temperature

I. Introduction

In a closed space such as the crewed space environment, monitoring of trace volatile organic compounds (VOCs) in the atmosphere is necessary to maintain the health of the crew and to prevent malfunctions of onboard equipment, and various analyzers have been developed.[1,2,3]

We have developed a portable gas chromatograph (GC) using ball surface acoustic wave (SAW) sensors,[4] ball SAW GC, with a volume of 1 L size and a weight of about 1 kg. [5] The ball SAW sensor is a small and highly sensitive sensor that utilizes multiple roundtrips of SAW on a spherical element. The ball SAW sensor can detect gases by measuring the change in characteristics of SAW when sample gas is adsorbed on the sensitive film coated on the sensor surface. Unlike other GC detectors, such as thermal conductivity detector, which require an additional reference gas, flame ionization detector, which requires fuel/oxidizer gases, and mass spectrometer, which requires an ion source, the ball SAW sensor requires none of them and can work only by installing in the end of the column. Therefore, the ball SAW sensor is useful in downsizing the GC system. This GC system uses a forward flush method[6] with two different columns to achieve separation difficult with a single column. A wide range of gases can be analyzed with a single system, and we have succeeded in separating and detecting multiple gases to be analyzed at the international space station (ISS). However, since this ball SAW GC uses a hydrogen storage canister as a carrier gas supply source, the canister needs to be replaced periodically. Therefore, we are developing a GC that uses air as the carrier gas and recirculates it to eliminate the need for canister replacement.

Previous prototypes using hydrogen gas as a carrier gas used a 20 m long 1701 column coated with 14% cyanopropylphenyl polysiloxane as a stationary phase and a 15 m long WAX column coated with polyethyleneglycol as a stationary phase for a total column length of 35 m.[5] On the other hand, when air is used as a carrier gas, air is more viscous than hydrogen, so the carrier gas flow velocity that achieves appropriate separation performance higher pressure is required to obtain adequate separation performance. However, since there is a limit to the ejection pressure of the circulation pump that can be applied in a portable GC, it is necessary to select a column that can effectively separate mixed gases with a total column length of about 20 m at maximum. In this study, the optimal column configuration was investigated by measuring multiple analytes analyzed at the International Space Station (ISS) using a combination of multiple columns with different column stationary phase thicknesses. Furthermore, we developed a prototype GC in which air was circulated as a carrier gas in the selected column combination and analyzed multiple components. In addition, by driving the ball SAW sensor at two frequencies, we demonstrated for the first time as a GC detector that the effect of sensor temperature and the response due to gas are separated in the measurement.

II. Measurement principle

In the ball SAW sensor, the velocity of the SAW that makes multiple roundtrips on the spherical element changes due to changes in the viscoelasticity of the sensitive film caused by the dissolution of gas in the sensitive film coated with the sensor surface. This change of the SAW velocity is detected as a delay time change (DTC) between the SAW excited by the interdigital transducer (IDT) on the sensor surface and received by the same IDT. However, DTC is also dependent on sensor temperature, and is therefore affected by changes in the environmental temperature of the sensor. However, if there is a sudden change in temperature for some reason, it is not possible to separate the effect of temperature from the response due to the gas concentration. To solve this problem, the use of two frequencies makes it possible to separate the effect of temperature from the effect of response due to gas.[7] In this chapter, we describe the measurement principle for separating the effect of temperature and response due to gas for a ball SAW sensor driven at two frequencies.

The DTC $\Delta t_1 = \Delta\tau_1/\tau_1$ at frequency f_1 and DTC $\Delta t_2 = \Delta\tau_2/\tau_2$ at frequency f_2 for a ball SAW sensor driven at two frequencies are respectively expressed as follows.

$$\Delta t_1 = B(T)f_1G(w) + A_1(T - T_{\mathrm{REF}}) \quad (1)$$

$$\Delta t_2 = B(T)f_2G(w) + A_2(T - T_{\mathrm{REF}}) \quad (2)$$

where τ_1 and τ_2 are delay time of SAW at f_1 and f_2. $B(T)$ is a sensitivity factor, w is a gas concentration, and $G(w)$ is a function of w. In the case of VOC sensor, it is known that $G(w) = w$ as previously reported.[8] T is a sensor temperature, T_{REF} is a reference temperature, and A_1 and A_2 are temperature coefficients at f_1 and f_2, respectively.

Assuming the temperature coefficient ratio (TCR) $C = A_2/A_1$, from $Eq.(2) - Eq.(1) \times C$, DTC depending on gas concentration can be obtained as

$$\Delta t_W \equiv \Delta t_2 - C\Delta t_1 = (f_2 - Cf_1)B(T)G(w). \quad (3)$$

For a sensor without a sensitized film, $A_1 = A_2$ and $C = 1$, whereas for a sensor with a sensitive film, the value varies close to 1.[7]

Similarly, from $Eq.(1) \times f_2/f_1 - Eq.(2)$, DTC due to temperature (temperature term) can be obtained as

$$\Delta t_T \equiv A_1(T - T_{\mathrm{REF}}) = \frac{(f_2/f_1)\Delta t_1 - \Delta t_2}{(f_2/f_1) - C}. \quad (4)$$

From the above, DTCs depend on gas concentration w and temperature T can be evaluated separately by using Eq. (3) and Eq. (4).

III. Design of ball SAW GC using air carrier gas

A schematic diagram of the ball SAW GC with air carrier gas installing the forward flush method is shown in Figure 1. This GC uses two columns CL1 and CL2 with different stationary phases and two ball SAW sensors BS1 and BS2 with different sensitive films. First, A purifier (PF) which is filled with adsorbents such as molecular sieve and active carbon to remove moisture and trace VOCs in the carrier gas is regenerated. To purge impurities from the adsorbent in PF, room air is passed though by a circulation pump (CP) for carrier gas while the PF is heated, as shown in Figure 1(a). Here, the buffer is a space larger than the flow piping to prevent the pump from inching. Next, after the temperature of the PF drops to around room temperature, the flow path is changed as shown in Figure 1(b) by switching the valves represented as open circles in the figure. The air carrier gas is circulated in the GC as shown in red line to remove the impurities at a pressure controlled by the pressure regulator (PR) with a proportionally controlled valve. At the same time, the sample gas containing components A-G and water vapor is vacuumed by a sample pump (SP) as shown in blue line and passed through a pre-concentrator (PC) filled with the adsorbent. For sample injection, CL1 and CL2 are connected in series as shown in Figure 1(c), and the sample gas adsorbed in the PC is injected by thermal desorption and introduced into CL1. Components A-C and water with low retention relative to CL1 are not separated and pass through BS1 and are introduced into CL2. On the other hand, components D-G, which have a large retention force relative to CL1, remain in CL1. In this state, switching to the parallel connection shown in Figure 1(d), components D-G are separated by CL1, detected in BS1, and then adsorbed in PF. Similarly, components A-C and water are separated by CL2, detected by BS2, and then adsorbed in PF.

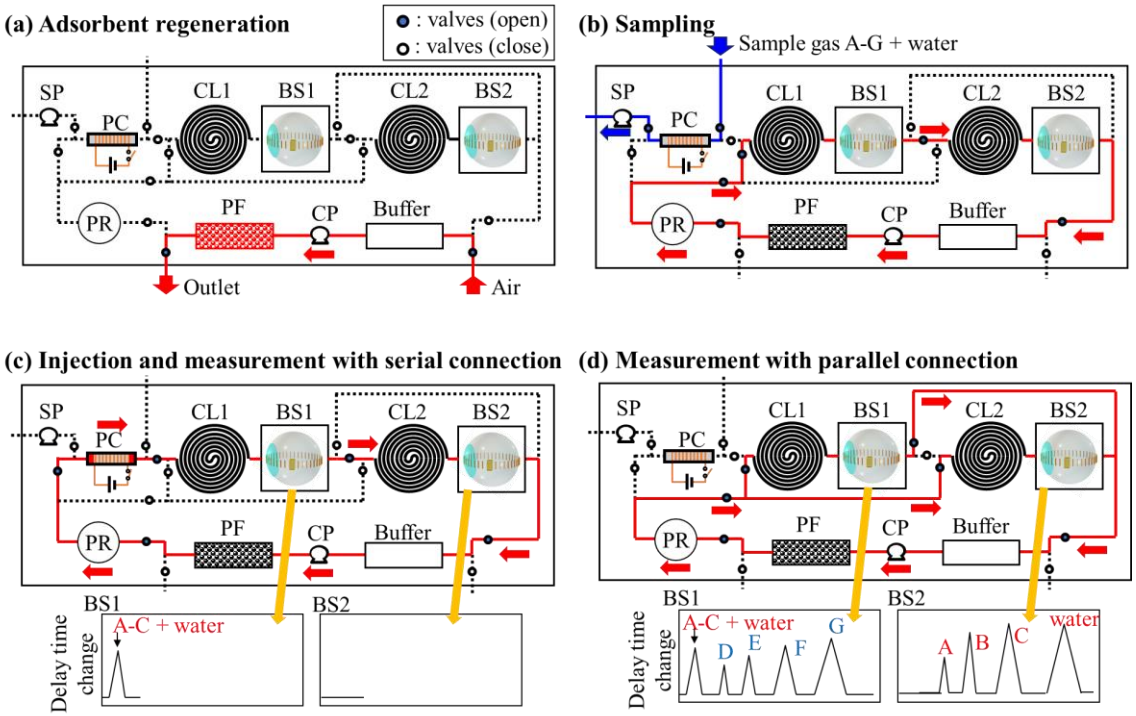
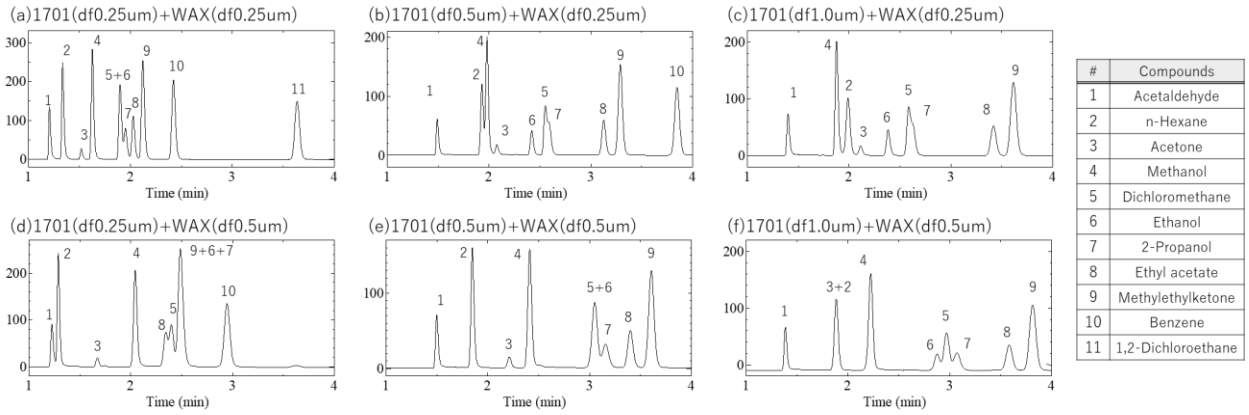


Figure 1. Schematic diagram of a portable GC using recirculated air as a carrier gas.

IV. Considerations of column combinations

Although the use of long columns is effective for improving the separation performance of multiple gases, the maximum column length that can achieve a practical column flow rate (about 20-35 cm/s with a column i.d. of 0.25 mm) at the discharge pressure of the circulation pump (about 70 kPa maximum) that can be installed in a portable GC is about 20 m. In previous studies, separation of gases to be analyzed in a crewed space environment has been achieved by a combination of a 1701 column coated with 14% cyanopropylphenyl polysiloxane as stationary phase and a WAX column coated with polyethyleneglycol 20M.[5] In this study, we investigated a combination of two columns with varying stationary phase thicknesses to achieve optimal separation performance. The columns were metal columns UltraALLOY (Frontier Laboratories Ltd.) with an inner diameter of 0.25 mm, cut to 10 m. Three types of 1701 columns with stationary phase thicknesses of 0.25, 0.5 and 1.0 μm were used, and two types of WAX columns with stationary phase thicknesses of 0.25 and 0.5 μm were used. Samples were prepared by selecting several components currently being analyzed on the ISS[9] that are considered difficult to separate and mixing them as a liquid sample. A desktop GC with a flame ionization detector (FID) was used to inject the liquid sample for measurement. Air supplied from a high-pressure cylinder was used as the carrier gas, with a carrier gas pressure of 67.5 kPa and a constant column temperature of 40°C.

The measurement results are shown in Figure 2. The chromatograms in three vertical rows represent the different stationary phase thicknesses of 1701, and the chromatograms in upper and lower lines represent the different stationary phase thicknesses of the WAX column. Each peak was confirmed by injecting a single component sample and identifying the retention time. The experimental results showed that the combination of a 1701 column with a stationary phase thickness of 1.0 μm and a WAX column with a thickness of 0.25 μm was most suitable for the separation of each component, as shown in Figure 2(c).



#	Compounds
1	Acetaldehyde
2	n-Hexane
3	Acetone
4	Methanol
5	Dichloromethane
6	Ethanol
7	2-Propanol
8	Ethyl acetate
9	Methylethylketone
10	Benzene
11	1,2-Dichloroethane

Figure 2. Comparison of column combinations by GC-FID.

V. Development of protype of ball SAW GC using air carrier

A prototype of a portable ball SAW GC with recirculated air carrier gas was developed with the combination of two columns selected in the previous section, as shown in Figure 3. Two metal columns, each 10 m longs, were each miniaturized into cylinder with the diameter of 3 cm and the length of 3 cm and wrapped by a heater wire. The purifier (PF) is 6 cm length 1/8" stainless tube filled with two different types molecular sieves. One adsorbs water and relatively low-boiling point VOCs such as ethanol and acetone, and the other adsorbs relatively high-boiling point VOCs such as toluene and xylene. All components were fixed on a single aluminum plate, measuring approximately 18 x 11 x 8.5 cm and weighing about 800 g. Note that the chassis is not included as it is currently being manufactured. The PC was a 1/16" stainless steel tube with an inner diameter of 1.2 mm filled with about 5 mm each of Tenax TA and Carboxen 1000 as absorbents. Combinations of columns and ball SAW sensors are shown in Table 1.

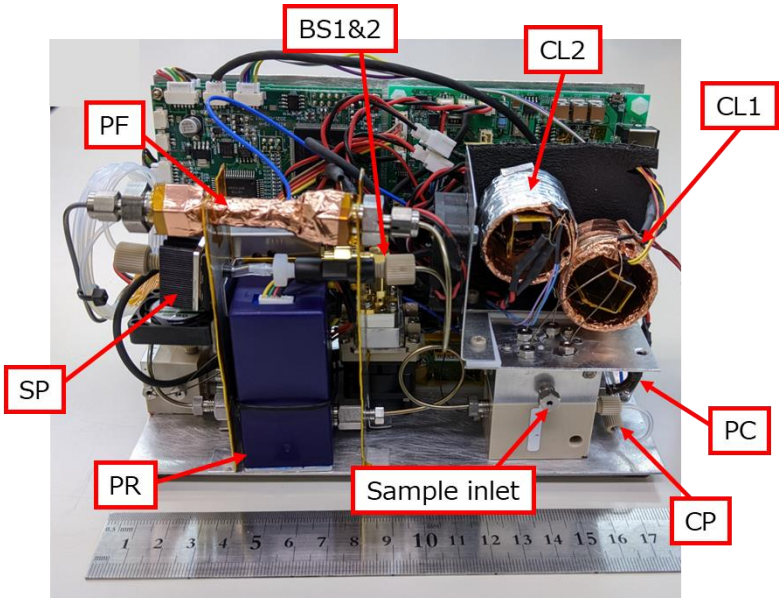


Figure 3. Prototype GC using air as a carrier gas.

Table 1. Columns (CL1 and CL2) and ball SAW sensors (BS1 and BS2) installed in the prototype GC.

	CL1	CL2
Stationary phase	14% Cyanopropylphenyl polysiloxane (1701)	Polyethylenglycol 20M (WAX)
Column length	10 m	10 m
Inner diameter	0.25 mm	0.25 mm
Thikness of stationary phase	1.0 μm	0.25 μm
	BS1	BS2
Sensitive film	Polydimethylsiloxane (PDMS)	Poly N-vinylpyrrolidone (PNVP)
Material	3.3 mm quartz	3.3 mm quartz
Frequency	f_1 = 80 MHz and f_2 = 150 MHz	f_1 = 80 MHz and f_2 = 150 MHz

For demonstration of the prototype GC, a sample gas mixture shown in Table 2 was prepared and analyzed. Since there was a still issue in separating all the gases used in the preliminary experiment shown in Fig. 2 by this prototype, we reselected gases that are easy to separate for this demonstration. The sample gas was prepared by injecting liquid samples into a nitrogen-filled gas sampling bag with a micro syringe and vaporizing them in the gas sampling bag. The sample gas was collected in the PC by the sample pump (SP) at 20 ml/min for 10 min as shown in Fig. 1 (b), and then injected by thermal desorption at 240°C in the serial mode as shown in Fig. 1 (c). The carrier gas pressure was increased from 30 kPa at 30 kPa/min and held at 60 kPa. The column temperature was held at 30 °C for 5 minutes for both CL1 and CL2, and then increased to 180 °C at 10 °C/min. Five minutes after the start of the measurement, the mode was converted to the parallel mode as shown in Fig. 1(d). During the measurement, the ball SAW sensor temperature was maintained at 30 °C by a Peltier device. The average power consumption of each stage is shown in Table 3.

Table 2. Composition of sample gas and their 180 day – SMACs.[10]

#	Compounds	180 day SMACs (ppmv)	Concentrations of sample mixture (ppmv)
1	Methanol	20	6
2	Acetone	22	6
3	Ethanol	1000	6
4	2-Propanol	60	6
5	Ethyl acetate	-	6
6	Benzene	0.07	2
7	n-Butanol	12	2
8	Toluene	4	1
9	m-Xylene	8.5	1
10	p-Xylene	8.5	1
11	o-Xylene	8.5	1

Table 3. Power consumption of the prototype GC.

Stage	Power consumption (W)
Regeneration	18.5
Sampling	14.3
Injection & measurement	18.8

The measurement results are shown in Figure 4. In the upper panel, a chromatogram with 150 MHz DTC Δt_2 is represented by the black curve and a chromatogram with 80 MHz DTC Δt_1 is represented by the blue curve. The middle panel shows the chromatogram of Δt_W obtained by subtracting Δt_1 from Δt_2 by Eq. (3), assuming the temperature coefficient ratio C =1. In the chromatograms of the individual frequencies (Δt_1 and Δt_2), there were baseline fluctuations. However, in the chromatogram of Δt_W, the baselines were stable, confirming the effect of removing the temperature effect. Furthermore, in the chromatograms of BS1, no distinct peaks were detected by 5 minutes of retention time before switching to parallel mode, but in the chromatogram of BS2, those components were separated and detected, confirming the effect of the forward flush method.

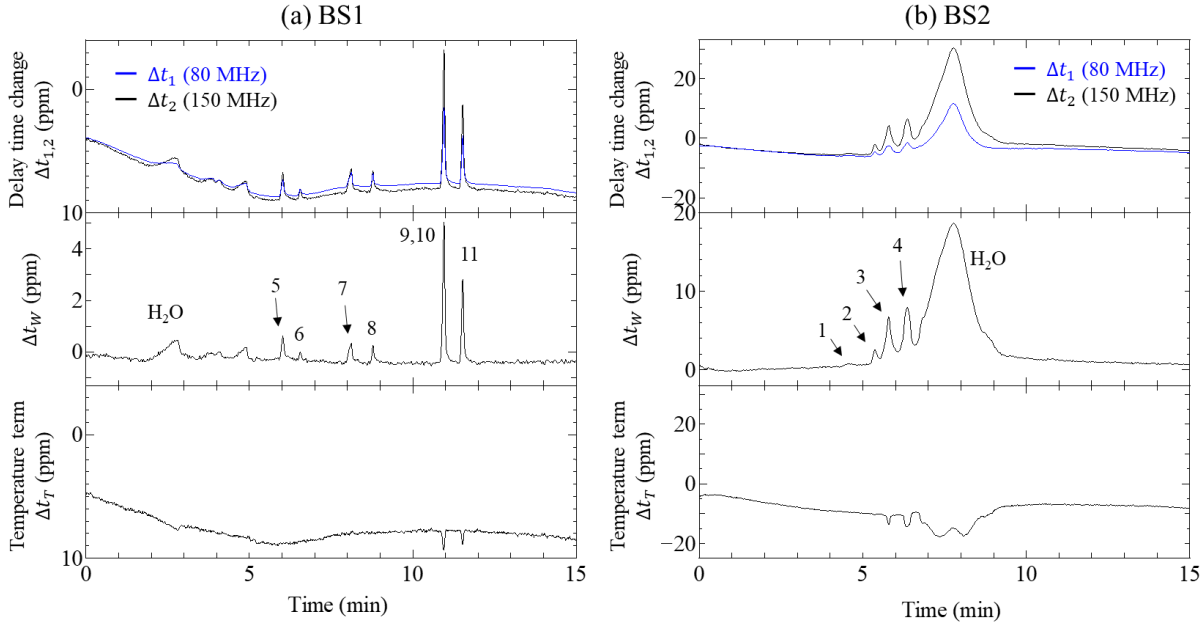


Figure 4. Chromatograms by the prototype GC. (a)BS1. (b) BS2.

The temperature terms calculated from Δt_1 and Δt_2 using Eq. (4) are shown in the lower panel. In the time variation of the temperature term, it changed negatively in conjunction with the response due to the gas. Since the temperature term contributes negatively to the sensor temperature,[7] the sample gas may have slightly increased the sensor temperature. While DTC using a single frequency may include the effect of the sensor temperature, by taking the difference between the responses of the two frequencies, only DTC by gas concentration changes can be evaluated. Therefore, the possibility of more accurate quantitative evaluation was demonstrated by the method of driving two frequencies.

In order to evaluate the gas concentration w from the chromatogram for Δt_W, it is necessary to create a calibration curve that shows the relationship between w and peak area or height of the chromatogram for each gas by measurements at several gas concentrations. We plane to create the calibration curve for each gas and evaluate performance such as detection limits, accuracy and repeatability of the protype, in the future work.

VI. Conclusion

A prototype ball SAW GC with air circulating as a carrier gas was developed to improve maintainability. To select the column to be mounted, the combination of stationary phase thicknesses of 1701 and WAX columns, which can efficiently separate gases to be analyzed at the ISS, was experimentally verified using GC-FID. Using the prototype, a wide variety of gases were analyzed and each component was successfully separated and detected. The ball SAW sensor was driven at two frequencies for the first time as a GC detector, showing the possibility of separating the effect of temperature from the response due to the gas. This is expected to enable more robust measurement against temperature changes in the surrounding environment.

In future research, we plan to evaluate the performance of this prototype, such as detection limits, and to verify its potential for use in future crewed space environments, as well as to identify application issues.

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References

[1]W. T. Wallace, T. F. Limero, K. W. Clark, and E. K. Hudson, and D. B. Gazda, “Effects of Ambient Alcohol Levels on the Real-time Monitoring of the Atmosphere of the International Space Station,” ICES-2022-57.

[2]M. Darrach, B. Bae, D. Fu, V. Garkanian, M. L. Homer, R. D. Kidd, C. Jung-Kubiak, H. Krause, F. Maiwald, S. Madzunkov, C. Malone, D. Nikolic, M. Rais-Zadeh, J. Simcic, T. Tillmans, and F. Zhong, “Calibration and Performance of the Spacecraft Atmosphere Monitor, an Air Constituent Monitor for Human Spaceflight,” ICES-2023-465.

[3]L. Pfeiffer, M. Gisi, E. Göhler, R. Seurig, A. Stettner, A. Honne, K. Kaspersen, K.A. Bakke, J. Thielemann, A.E. Liverud, and P. Rebeyre, “ANITA-2 – the Advanced Multicomponent Air Analyser for ISS – First Year of Operation, Hardware Behaviour, Expected Lifetime and Reliability as well as Future Updates for ANITA-3,” ICES-2023-92.

[4]K. Yamanaka, H. Cho, and Y. Tsukahara, “Precise velocity measurement of surface acoustic waves on a bearing ball,” Appl. Phys. Lett., Vol. 76, No. 19, 2000, pp. 2797-2799.

[5]T. Iwaya, S. Akao, K. Yamanaka, T. Okano, N. Takeda, Y. Tsukahara, T. Oizumi, H. Fukushi, M. Sugawara, T. Tsuji, T. Tanaka, A. Takeda, A. Shima, S. Matsumoto, H. Sugahara, T. Hoshino, and T. Sakashita, “Development of Portable Gas Chromatograph Using Ball Surface Acoustic Wave Sensor for Measurement of Crewed Space Environment,” ICES-2022-172.

[6]Y. Yamamoto, S. Akao, H. Nagai, T. Sakamoto, N. Nakaso, T. Tsuji, and K. Yamanaka, “Development of Multiple-Gas Analysis Method Using the Ball Surface Acoustic Wave Sensor,” Jpn. J. Appl. Phys., Vol. 49, 2010, 07HD14.

[7]K. Yamanaka, S. Akao, N. Takeda, T. Tsuji, T. Oizumi, and Y. Tsukahara, “Simultaneous measurement of gas concentration and temperature by the ball surface acoustic wave sensor,” Jpn. J. Appl. Phys. Vol. 56, 2017, 07JC04.

[8]S. Akao, N. Iwata, M. Sakuma, H. Ohnishi, K. Noguchi, T. Tsuji, N. Nakaso, and K. Yamanaka, “Development of Microseparation Column for Ball Surface Acoustic Wave Gas Chromatograph”, Jpn. J. Appl. Phys. Vol. 47, 2008, 4086-4090.

[9]W. T. Wallace, T. F. Limero, L. J. Loh, P. D. Mudgett and D. B. Gazda, “Monitoring of the Atmosphere on the International Space Station with the Air Quality Monitor,” ICES-2017-103.

[10]V. E. Ryder, “Spacecraft Maximum Allowable Concentrations for Airborne Contaminants,” JSC 20584, April 2020.