Infrared spectral radiometer: A new tool for remote measurement of SO₂ of volcanic gas

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We have determined SO₂ concentration in fumarolic gas released from the summit crater of Asama volcano, Japan, using an infrared spectral radiometer installed in a site about 4 km away from the summit. During the observation period from 31 October to 4 November 1991, weak fumarolic activities with a height less than 100 m were observed intermittently. The infrared spectrum of the fumarolic gas just above the summit showed slight absorption due to rotational bands associated with ν_1 vibration (1151 cm⁻¹) of the SO₂ molecule. Compared with the spectrum of standard SO₂ gas, this absorption corresponds roughly to the column amount of 250 ppm-m SO₂. This is the first result of remote detection of SO₂ in volcanic gas from a ground station by means of infrared spectroscopy. Infrared spectral radiometer is a promising tool for remote detection of various chemical species in volcanic gas.

INTRODUCTION

Matsuo (1975, 1979) said "Volcanic gas is a telegram from the earth's interior", analogizing a famous saying in Japan "Snow is a letter from the sky" by Dr. Ukichiro Nakaya. As volcanic gas originates from volatile components dissolved in magma, its chemical compositions can give direct information on the nature of magma which is generated in the upper mantle or lower crust.

The temporal variation in chemical composition of volcanic gas is thought to reflect changes in the condition of the magma; i.e. changes in temperature and/or pressure of the magma and the gas separated from the magma, changes in degassing rate of the magma, and chemical reaction between gas components and surrounding materials. Until present, a number of observations showing changes in chemical composition of volcanic gas prior to volcanic eruptions have been reported, as reviewed by Hirabayashi (1985). The chemical composition of volcanic gas is usually measured using a combined

method of wet chemical analysis and gas chromatography (Notsu, 1984; Hirabayashi, 1986). In order to monitor chemical composition of volcanic gas, gas samples must be collected and analyzed periodically. It is, however, difficult to collect gas samples around the summit crater when volcanic activity becomes high. This is why a remote sensing technique was chosen to measure the chemical composition of volcanic gas.

A Barringer correlation spectrometer (COSPEC) is a remote sensing device for determining SO₂ flux of volcanic gas from ground base or airborne platforms using absorption bands in the ultraviolet region around 0.3 μ m. This method was originally developed for monitoring air-pollution of industrial origin and has later been applied to remote observation of volcanic gas since the early 1970's (Stoiber and Jepsen, 1973). In the case of 1991 eruptions of Pinatubo volcano, the Philippines, anomalous change in SO₂ flux based on COSPEC data just before the big eruptions on 12 to 15 June was one of the key observations for PHIVOLCS

(The Philippine Institute of Volcanology and Seismology) to issue an alert announcement (Smithsonian Institution, 1991). Sulfur dioxide absorption features in the ultraviolet region are also used for SO₂ measurements in the stratosphere after large, explosive eruptions using the Total Ozone Mapping Spectrometer (TOMS) installed on a satellite which encircles the Earth (Krueger, 1983).

Besides ultraviolet spectroscopy, infrared spectroscopy has not been used routinely for the remote measurement of chemical species in volcanic gas. Only a few attempts have been carried out. Naughton *et al.* (1969) observed the infrared absorption of the gas and fume being evolved from the lava fountain at Kilauea volcano, Hawaii. Realmuto *et al.* (1992) determined the SO₂ concentration and the flux from Etna volcano, Italy, using image data acquired with NASA's airborne Thermal Infrared Multispectral Scanner (TIMS).

At present, remote sensing techniques to determine other species than SO₂ in volcanic gas are not widely available. In this work, we try to develop a new technique for remote chemical monitoring of volcanic gas on the basis of infrared spectroscopy.

INFRARED SPECTRAL RADIOMETER

Volcanic gas consists mostly of water vapor (H₂O) with the content of more than 95 volume % in many cases. The major species, excluding H₂O, are usually CO₂, SO₂, H₂S and HCl. Other species such as H₂, HF, N₂, Ar, CH₄ and CO are usually minor constituents (Matsuo, 1975, 1979).

The frequencies (or wavelengths) of normal vibrations of these gaseous species are in the infrared region. In addition, there are a series of rotational states around the frequency of each normal vibration. If an infrared light source is available, it is expected that these species will be detected by their absorption of the infrared, analogous to conventional infrared spectroscopy in the laboratory. Ambient light, which is ultimately from the sun, can be the light source. This means that the infrared spectroscopy will be

applied to remote multi-components analyses of volcanic gas, in contrast to the ultraviolet spectroscopy such as COSPEC or TOMS for the determination of SO₂ only. A similar type of infrared absorption measurement has been already conducted to determine stratospheric trace gases from airborne (Mankin and Coffey, 1983) and ground-based platforms (Rinsland *et al.*, 1991).

When the infrared spectrum of the volcanic gas is obtained through the surface air, atmospheric H₂O (the concentration is variable around 0.5%) and CO₂ (about 340 ppm) along the optical path may interfere significantly with the absorption spectrum of the volcanic gas. Thermal condition of volcanic gas, volcanic body and atmosphere may modify the absorption features of volcanic gas. The absorption coefficients of gaseous species depend on the temperature. In some cases, the thermal radiation from the volcanic body may be an infrared light source.

In this work, a portable Fourier-transform infrared (FT-IR) spectral radiometer with double port interferometer (Bomen Co. model MB100-2E) was used. Infrared radiation through the fumarolic gas is focussed with a Cassegrain-type telescope (field of view: 5 mrad., diameter of mirror: 25 cm) and is introduced into the interferometer through the 1st input port. As the 2nd input port is closed with the shutter from the external light, the thermal radiation from the shutter with room temperature is introduced into the interferometer through the 2nd input port. The optical subtraction of these two input signals is recorded with a FT-IR spectral radiometer operating at 1 cm⁻¹ resolution. In this observation, an MCT (Mercury-Cadmium-Tellurium) detector with maximum sensitivity in 1000 to 1200 cm⁻¹ region was used.

OBSERVATION ON ASAMA VOLCANO

Asama volcano (36°24'N, 138°31'E, 2560 m above sea level) is one of the active volcanoes in Japan and has erupted frequently in historic times (Aramaki *et al.*, 1981; Smithsonian Institution, 1981). The latest eruption occurred on 20

July 1990 and the daily maximum height of the fumarolic gas from the summit crater exceeded 1500 m in August of the same year. After the eruption, the fumarolic activity has been decreasing and the daily maximum height of the fumarolic gas was 100 m or less in our observation periods on 31 October and 1 November 1991 (Japan Meteorological Agency, unpublished data).

The SO_2 emission rate has been measured periodically since 1977 using a COSPEC by Ohta *et al.* (1988), who reported the enhancement of SO_2 emission prior to the 1982–1983 eruptions. The emission rate of SO_2 from Asama volcano is estimated to be more than 500 t/day during the eruptive stage and less than 300 t/day during the calm stage. Earlier work by Noguchi and Kamiya (1963) reported that the S/Cl ratio of fumarolic gas collected on the northeastern side of the crater rim increased few months prior to the 1958 eruption.

Figure 1 is a map showing our observation site on the northern flank of Asama volcano. The horizontal distance between the observation site and the summit crater where fumarolic gas is emitting is about 4 km, and the difference of the altitudes is about 1150 m.

Figure 2 is a photograph of fumarolic gas emitted from the summit crater. During our observation period, the fumarolic gas was observed to release not continuously but intermittently. After emission, the gas rose and seemed to disappear within tens of meters above the summit. Therefore, as soon as the fumarolic gas was observed to be emitted, the FT-IR spectrometer was operated, adjusting the focus of the telescope to the lower part of the fumarolic gas. In this observation, infrared radiation from the area with a diameter of about 20 m was analyzed. Because the fumarolic gas target is moving and dissipates easily within the standard analyzing time (about 8 minutes), it took many trials to obtain each infrared spectrum of the fumarolic gas. Therefore, total 11 spectra of the fumarolic gas were obtained from observations during the 2 days described previously.

Fig. 1. Locations of observation site and summit crater of Asama volcano where fumarolic gas is emitting.

Fig. 2. Photograph of fumarolic gas emitting from the summit crater of Asama volcano (taken on 31 July 1991). An angular block on the left side of the fumarolic gas is a volcanic block with 23 m long, 10 m wide and 12.5 m high, so called "Senton-iwa", which was ejected at the time of the explosion on 23 Sep. 1950.

RESULTS AND DISCUSSION

Figure 3 is a typical example of the infrared spectrum of the fumarolic gas (Trial 13) between 800 and 2500 cm^{-1} . This spectrum is a raw output of the MCT detector, without correction of

Fig. 3. Infrared spectrum ($800\text{--}2500\text{ cm}^{-1}$) of fumarolic gas (Trial 13) emitting from the summit crater of Asama volcano.

Fig. 4. Infrared spectrum ($1100\text{--}1200\text{ cm}^{-1}$) of fumarolic gas (Trial 13) and background (Trial 14). Trial 14 spectrum is drawn by shifting $+0.2$ of the vertical axis unit not to cross the two spectra. Absorption bands due to SO_2 are indicated as arrows.

the sensitivity of the detector dependent on the frequency. The expanded spectrum of the Trial 13 in the range between 1100 and 1200 cm^{-1} is shown in Fig. 4. In this figure, the infrared spectrum of the sky near the fumarolic gas, which was measured next to the Trial 13, is also shown as a background spectrum (Trial 14). During the observation periods, the weather condition was not good: the sky was always covered with thick clouds. Therefore, the background spectrum represents infrared radiation from the clouds beyond Asama volcano. When we observe absorption features in the infrared spectrum of the fumarolic gas, infrared radiation from the clouds is thought to be the light source.

The general features of both spectra shown in Fig. 4 are very similar to each other. Major absorption bands observed in both spectra are due to water vapor (H_2O). However, there are several small absorption bands among major H_2O absorption bands in the fumarolic gas spectrum (Trial 13), which are not found out in the background spectrum (Trial 14). In order to display the absorption features of the fumarolic gas, the ratio of the fumarolic gas against the background radiation, defined as (Trial 13/Trial 14), is shown in Fig. 5. An absorption spectrum of SO_2 obtained in our laboratory using the same MB100 spectrometer with a resolution of 1 cm^{-1} is also shown in Fig. 5. In the spectrum of the fumarolic gas, absorption bands due to rota-

Fig. 5. Ratio of fumarolic gas against background sky radiation (Trial 13 / Trial 14) (lower spectrum) and standard SO_2 gas (upper spectrum). Absorption bands due to SO_2 are indicated as arrows.

tional states of ν_1 vibration (1151 cm^{-1}) are clearly identified, though it includes other absorption features than SO_2 , possibly due to H_2O .

When we compare the absorbance of the assigned SO_2 bands in the spectrum of the fumarolic gas with that of $1650\text{ ppm}\cdot\text{m}$ of standard SO_2 gas, we can calculate the column amount of SO_2 across the fumarolic gas to be approximately $250\text{ ppm}\cdot\text{m}$. Assuming that the fumarolic gas is rising with a diameter of about 50 m just above the summit crater, the concentration of SO_2 in the fumarolic gas is about 5 ppm .

Fig. 6. Infrared spectra ($2700\text{--}3050\text{ cm}^{-1}$) of fumarolic gas (Trial 13) (lower spectrum), background (Trial 14) (middle spectrum) and standard HCl (higher spectrum).

Other spectra obtained in this work are nearly the same as Trial 13 spectrum. Only small absorptions due to SO_2 are variable and their absorbances are estimated to be similar to or less than that of Trial 13. Considering that the volcanic gas moves easily outside the field of view of the telescope, Trial 13 may be an optimum observation.

Another candidate to be detected in the infrared absorption spectrum of the fumarolic gas is HCl. HCl has absorption bands due to rotational states associated with vibration (2886 cm^{-1}) in the region between 2600 and 3100 cm^{-1} . Figure 3 shows that the infrared radiation of the fumarolic gas is very low above 2500 cm^{-1} , even though the low sensitivity of the MCT detector in this frequency region is considered. In Fig. 6, the expanded spectra of the fumarolic gas (Trial 13) and background (Trial 14) in the range $2700\text{--}3050\text{ cm}^{-1}$ are shown, together with the absorption feature of HCl. Both spectra of Trial 13 and Trial 14 are similar and very noisy near zero level detector counts. It is difficult to recognize HCl bands in the fumarolic gas spectrum (Trial 13). In this observation, the light source around 3000 cm^{-1} is too weak to obtain the absorption spectrum of HCl, even if a detectable amount of HCl is released. In the case where the HCl column amount of the volcanic gas is above 100 ppm-m and an adequate light source around

3000 cm^{-1} is available, it may be possible to detect HCl bands. Infrared spectral radiometer is a promising tool for remote monitoring of HCl/ SO_2 ratio of volcanic gas.

SUMMARY

Infrared radiation of the fumarolic gas emitting from the summit of Asama volcano was observed using an infrared spectral radiometer installed about 4 km apart from the summit. Absorption bands due to SO_2 were identified and the column amount was estimated about 250 ppm-m . This is the first result of remote determination of SO_2 in volcanic gas from a ground station by means of infrared absorption. This method will be applicable to other chemical species in the future.

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