



Monitoring atmospheric ^{85}Kr by atom counting

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ABSTRACT

Radioactive ^{85}Kr is a major gaseous fission product emitted into the air by the nuclear fuel reprocessing industry. Measuring atmospheric ^{85}Kr has applications in environmental monitoring, atmospheric transport model validation and dating of environmental water samples, including groundwater, sea water and glacier ice. We present an ultra-sensitive method for fast analysis of atmospheric ^{85}Kr at 10^{-5} parts per trillion level. This method is based on laser cooling and trapping and is capable of counting individual ^{85}Kr atoms. Measurements at the 3% precision level can be made on krypton extracted from 1L STP of air with a turnaround time of 1.5 h. Moreover, we have realized a system for continuous air sampling over days to weeks. Based on this atom-counting technology and a portable air sample integrator we have realized atmospheric ^{85}Kr baseline monitoring in Hefei, China, for over 20 months. The technological advances presented in this work lay the ground for a global atmospheric ^{85}Kr monitoring network.

1. Introduction

^{85}Kr is a radioactive isotope present in the atmosphere. Its half-life is 10.74 years (Singh and Chen, 2014). Although it can be produced naturally, the dominant source since 1950 has been anthropogenic (Minski, 1993; Rózański, 1979; Sittkus and Stockburger, 1976). Its concentration in the air is extremely low, at the level of 10^{-5} ppt (parts per trillion, the isotopic abundance is 10^{-11}). Currently its activity in the air is about 1.5 Bq/m^3 (Bollhöfer et al., 2019; Kersting et al., 2020a and 2020b). Today the largest ^{85}Kr emission sources are the nuclear fuel reprocessing plants in the UK and France (Ahlsvede et al., 2013). The global distribution of ^{85}Kr is relatively even except in central Europe where large heterogeneities are present due to the proximity to the sources and the local weather patterns (Ross, 2010). Since the ^{85}Kr emission sources are all located in the northern hemisphere and the inter-hemisphere exchange time is 1–2 years, the atmospheric concentration of ^{85}Kr is 15–20% lower in the southern hemisphere (Bollhöfer et al., 2014, 2019; Ross, 2010). Monitoring atmospheric ^{85}Kr concentration is important for several reasons: 1) The monitoring data can be used to evaluate potential impacts on human health and the environment (Igarashi et al., 2001; Ross, 2010; Scott Kemp, 2008). 2) Being a

chemically inert gas with a suitable half-life, ^{85}Kr is a good tracer for dating young groundwater and is used to monitor wells for drinking water (Althaus et al., 2009; Avrahamov et al., 2018; Cook and Solomon, 1995; Ekwurzel et al., 1994; Kagabu et al., 2017; Lehmann et al., 1991; Smethie et al., 1992). Such applications need the knowledge of the ^{85}Kr input function which can be inferred from the atmospheric ^{85}Kr concentration record in the region under study (Bollhöfer et al., 2019; Kersting et al., 2020a and 2020b). 3) It can be used to validate atmospheric transport models or investigate atmospheric and inter-hemispheric transport processes (Bollhöfer et al., 2014; Kjellstrom et al., 2000; Levin and Hesshaimer, 1996; Ross, 2010; Zimmermann et al., 1989). 4) A global ^{85}Kr monitoring network may have potential applications for treaty verification purposes (Kalinowski et al., 2004; Schoepfner and Glaser 2016).

The commonly used method for measuring atmospheric ^{85}Kr activity is proportional counting. Due to the extremely low concentrations of ^{85}Kr in the atmosphere, large amount of air sample (10 m^3 in one week) needs to be processed by cryogenic distillation and gas chromatography before the resulting krypton can be counted in a proportional counter system (typically for 1 h) (Cimbák and Povinec, 1985; Schlosser et al., 2017). It is possible to measure smaller air samples (a few liters) in

Abbreviations: ATTA, Atom Trap Trace Analysis; LLC, Low-Level Counting.

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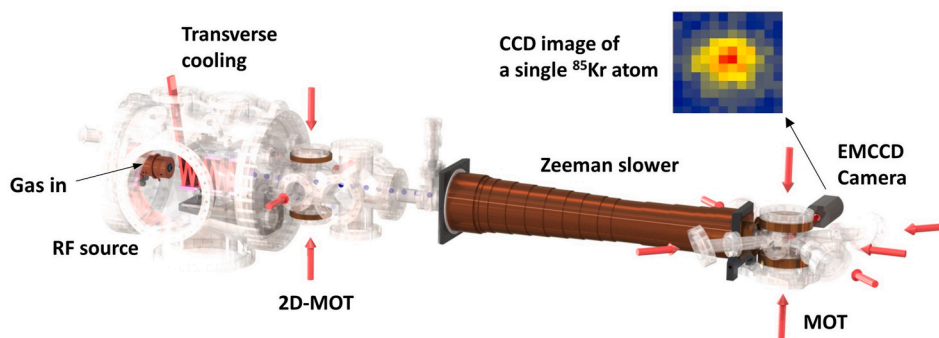


Fig. 1. Schematic of the Atom Trap Trace Analysis apparatus for atmospheric ^{85}Kr concentration measurement. MOT: Magneto-optical trap; 2D-MOT: 2-Dimensional Magneto-optical trap. The red arrows represent various of laser beams used for manipulation of atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

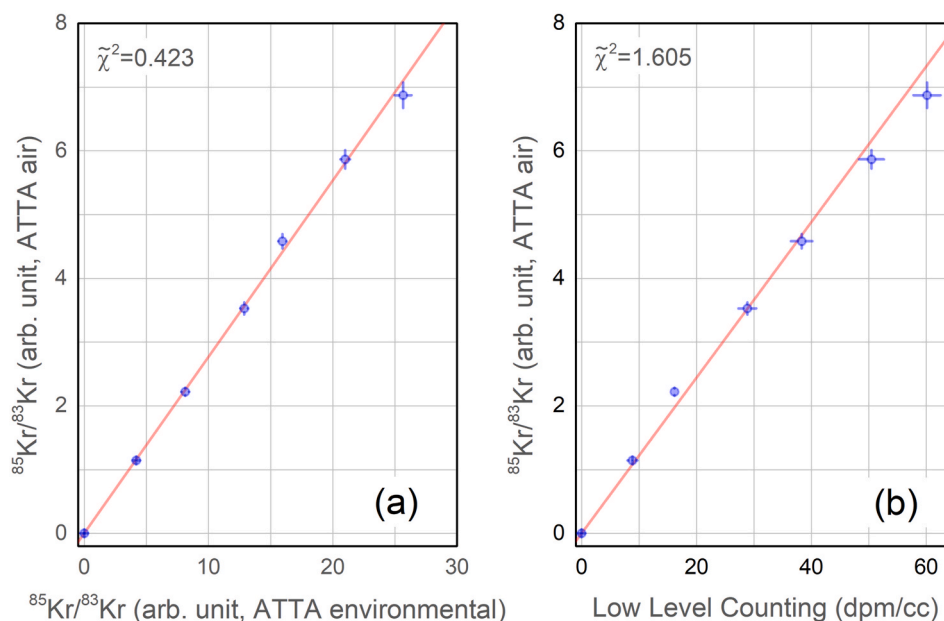


Fig. 2. (a) Comparison of $^{85}\text{Kr}/^{83}\text{Kr}$ ratios measured by two independent ATTA apparatus (see text for details). (b) Comparison of $^{85}\text{Kr}/^{83}\text{Kr}$ ratios measured by ATTA and LLC.

underground low level counting laboratories. However, the measurement time is long (a few days), which limits the throughput (Collon et al., 2004; Loosli and Purtschert, 2005). The emerging Atom Trap Trace Analysis (ATTA) method is a good candidate for measuring the ^{85}Kr activities of small air samples (liters) quickly (Chen et al., 1999; Dong et al., 2019; Jiang et al., 2012; Zappala et al., 2017). ATTA is based on the laser cooling and trapping technique. In ATTA the ^{85}Kr atoms are selectively captured by a resonant laser trap and counted by monitoring their fluorescence. Thanks to the resonance nature of this method, it is extremely selective and sensitive. It is capable of detecting isotopes at the 10^{-17} isotopic abundance level. Analysis of ^{85}Kr in environmental samples with ATTA has been realized (Yang et al., 2013; Zappala et al., 2017). In this paper we present fast analysis of ^{85}Kr activities in air samples based on the ATTA method. An ATTA apparatus has been developed for the air sample measurement. Measurements at the 3% precision level on a 1 L STP (Standard Temperature and Pressure) air sample have been realized with 1.5-h turnaround time. Moreover, we have realized a system for continuous air sampling over days to weeks. Based on these novel instrumental advances, data from monitoring atmospheric ^{85}Kr in the city of Hefei, China, with weekly resolution for more than twenty months is presented.

2. Materials and methods

In developing the ATTA apparatus for fast analysis of ^{85}Kr , we recognize that the isotopic abundance of ^{85}Kr in the air and environmental water samples are quite different. In environmental samples, like groundwater, the isotopic abundance of ^{85}Kr can vary by many orders of magnitude, from 10^{-11} to below the detection limit (6×10^{-14}). On the other hand the relative fluctuation of ^{85}Kr activity in the air is much smaller, between 1.4 and 3.0 Bq/m^3 (corresponding to isotope abundance of 2.3×10^{-11} to 5.0×10^{-11}) in most parts of the world except for the places near the emission sources (Bollhöfer et al., 2019).

The ATTA apparatus reported in previous works are all aimed at measuring environmental samples, where both high detection efficiency and small cross-sample contamination are critical due to the large variation of the isotopic abundance of ^{85}Kr (Jiang et al., 2012, 2020; Yang et al., 2013). To achieve high efficiency part of the system needs to be cooled to 130 K, which causes more adsorption and implantation of the Kr sample. As a result, after each measurement, the vacuum system of the apparatus needs to be cleaned thoroughly with a Xe discharge for at least 10 h to suppress the memory effect (Jiang et al., 2020). This long turnaround time cannot meet the demand from high-throughput applications, such as atmospheric ^{85}Kr monitoring. Operating an ATTA

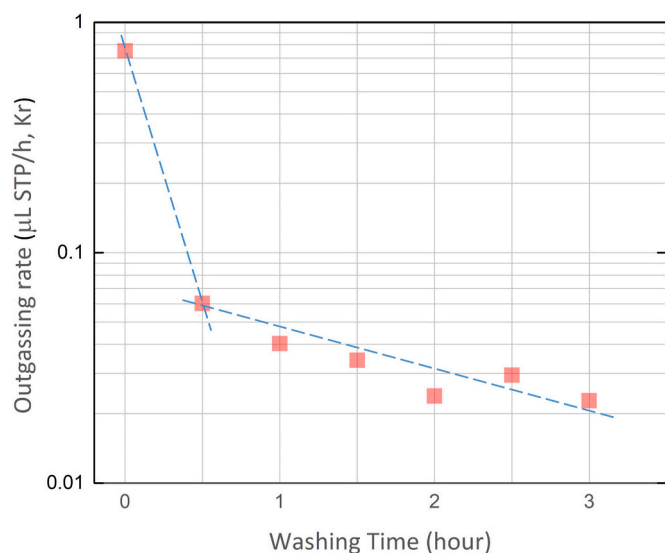


Fig. 3. Outgassing rate vs. washing time. The data are averages of two separate measurements. Dash lines are a guide to the eye.

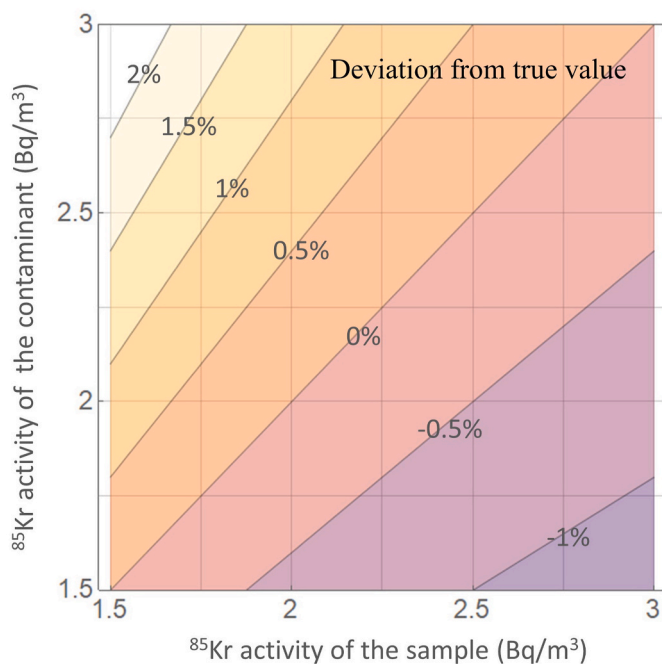


Fig. 4. The calculated contour plot of the relative deviation from the true ^{85}Kr activity of the sample due to the cross-sample contamination effect. The horizontal axis is the ^{85}Kr activity of the sample. The vertical axis is the ^{85}Kr activity of the contaminant.

apparatus for environmental samples near room temperature with a reduced turnaround time (4 h) was reported. However the atom count rate was compromised under using those working parameters. As a result the sample size is limited to 5–10 μL STP of Kr (Zappala et al., 2017).

To reconcile these problems we designed an ATTA apparatus for atmospheric ^{85}Kr concentration measurement, modified the parts to reduce memory effect and tailored a measurement protocol with short turnaround time.

The main structure of the apparatus is shown in Fig. 1. It has a discharge source producing metastable Kr atoms, atomic optics along the way to collimate and slow down the atomic beam and a magneto-

optical trap for trapping and analyzing the ^{85}Kr isotope (Chen et al., 2001; Jiang et al., 2012). Laser trapping and cooling of krypton atoms are achieved by resonantly exciting the cycling transition $5s[3/2]_2 - 5p[5/2]_3$. The $5s[3/2]_2$ state is metastable, and is populated with an efficiency of $\sim 10^{-4}$ by sending the sample gas through a RF-driven discharge source (Chen et al., 2001; Jiang et al., 2012). A diverging beam of metastable atoms is collimated in a 20 cm long, two-dimensional transverse cooling zone. The forward atomic beam flux is enhanced by a factor over 100. A two-dimensional trap is used to focus the already collimated atomic beam, thus boosting the trap capture efficiency further. A 2 m long Zeeman slower, containing a reverse-biased segment near the MOT (Magneto-optical trap), improves the transition of atoms from the slower into the trap, and has a capture velocity of 500 m/s. Analyzing a 1 μL STP atmospheric krypton sample, the new ATTA apparatus can capture ^{85}Kr (I.A. $\sim 10^{-11}$) at the rate of 3000 atoms per hour. A sensitive EMCCD (Electron Multiplying Charge Coupled Device) camera is used to record both the spatial and intensity information of the fluorescence image of the trapped atoms. The intensity of the fluorescence can be used to determine the number of the ^{85}Kr atoms in the trap.

One of the key improvements of the ATTA apparatus is the discharge source operating at room temperature. It can reduce the adsorption of sample and eliminate the time to cool down and warm up the system in the cleaning process. As a result the system cleaning time can be shortened to 1 h. However, the higher operating temperature will result in a more divergent metastable Kr atomic beam with a higher longitudinal temperature, which will cause a reduction of detection efficiency. To compensate this problem, a 2 m long Zeeman slower with a high capture velocity (500 m/s) is installed. With these changes, high ^{85}Kr count rates for Kr extracted from air samples (~ 3000 atoms/h for 1 μL STP Kr) are achieved.

Besides the hardware improvements, a tailored measurement protocol is also developed to allow fast ^{85}Kr analysis on air samples. For air sample ^{85}Kr analysis, the Kr is first extracted from 1 L STP of air and then analyzed by the ATTA method. The krypton extraction method has been established and reported (Dong et al., 2019). There are three major steps in the extraction process. First the reactive gases (O_2 , N_2 etc.) are removed by hot Titanium-sponges in an oven. The residual gases (mostly Ar and Kr) are then sent through a GC (gas chromatography) for separating Kr from Ar. In the final step, a getter pump is used to remove the remaining trace amount of reactive gases from Kr. The purified Kr is analyzed by ATTA. In the following we will focus on the ATTA analysis protocol, the precision of the measurement and the effect of the cross-sample contamination.

First the ATTA apparatus is calibrated with the traditional Low-Level Counting (LLC) method. An inter-comparison between two ATTA apparatus (the ATTA apparatus for air measurement and another ATTA apparatus for environmental samples in our lab) is also conducted. A series of standard ^{85}Kr samples with different concentrations are measured by the two ATTA apparatus and LLC separately. The result is shown in Fig. 2. Good linear relationships are found among the two independent ATTA apparatus and the LLC. This demonstrates the ability to perform quantitative analysis.

To establish the protocol for measuring air samples, we studied the memory effect of the ATTA apparatus. After measuring the sample, the vacuum system is washed by a xenon (ultra-high purity grade, 99.999%, Kr < 2 ppm) discharge. The discharge is sustained by a helical coil driven by a RF amplifier with 20 W power. The outgassing rate of the vacuum system after different cleaning time is measured and depicted in Fig. 3. As expected, the Kr outgassing rate decreases sharply with the washing time, thanks to the low adsorption and implantation of the room temperature discharge source. Within 1 h the outgassing rate drops to less than 0.1 μL STP/h (Kr). This is significantly faster than the low temperature ATTA apparatus which will need 8–10 h of wash to reach the same outgassing rate (Jiang et al., 2020). Based on the outgassing rate measurement we designed a protocol for air sample ^{85}Kr activity measurements. Each ATTA analysis of air sample (0.5 h) is

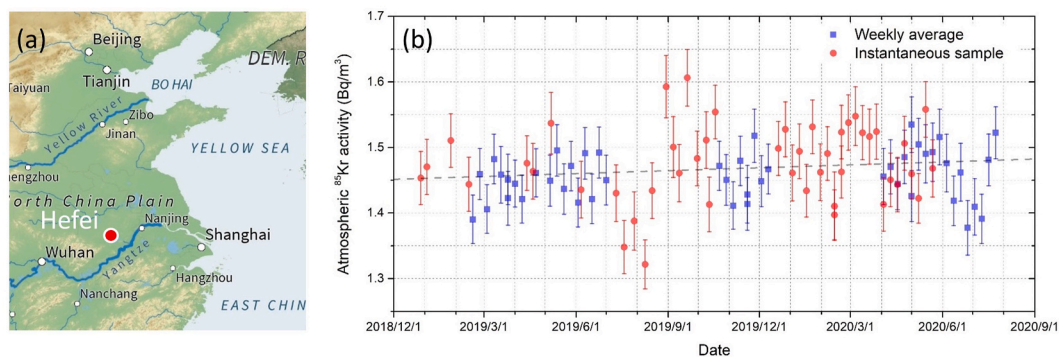


Fig. 5. (a) Location of the sampling site (Hefei, China). The map comes from [mapswire.com](https://www.mapswire.com) under Creative Commons license. (b) Atmospheric ^{85}Kr activity in Hefei from Dec. 2018 to Aug. 2020. The gray dash line is the linear fit of the data. The slope is $0.018 \pm 0.011 \text{ Bq/m}^3/\text{year}$. Data points with same date are duplicate measurements. They agree with each other within error bars.

followed by a 1-h system cleaning. This sample measuring sequence is repeated and an ^{85}Kr reference sample is measured at the end of the sequence (commercial Kr sample purchased in 2018; The ^{85}Kr activity is measured to be $64.3 \pm 0.04 \text{ dpm/cc}$ on October 2nd 2019). Under this protocol the turnaround time for analyzing each air sample is reduced to 1.5 h. So 4–5 samples can be analyzed in an 8-h shift. In the following we will discuss the cross-sample contamination effect under this measurement protocol and show it is negligible compared to the current measurement precision.

The ATTA analysis of a typical air sample takes 0.5 h (1 L STP air or 1 μL STP Kr, 3% precision). After 1-h of xenon wash the typical outgassing rate is below 0.1 μL STP/h (Kr), the average volume fraction of the contamination will be less than 2.5% in the 0.5 h ATTA measurement. However, the effect of cross-sample contamination depends not only on the contamination volume fraction but also on the ^{85}Kr concentration difference between the sample and the contaminant. To evaluate the effect of cross-sample contamination we consider how the atmospheric ^{85}Kr activities vary around the world. According to previous studies, the variation of the weekly average of ^{85}Kr concentration in the air in a given location is normally less than 20% except in Europe where larger variations are observed due to the ^{85}Kr sources located in France and UK (Bollhöfer et al., 2019; Ross, 2010). We therefore use typical parameters in Europe to estimate cross contamination, since concentration differences in samples from there are larger compared to other regions in the world. The ^{85}Kr baseline in central Europe is relatively flat and the concentration from 2014 to 2019 is about 1.5 Bq/m^3 (Bollhöfer et al., 2019). The weekly average of ^{85}Kr concentration, however, shows many spikes above the baseline. We notice that the peak values are mostly below 3 Bq/m^3 except for a few points (Bollhöfer et al., 2019). So in estimation of the cross-sample contamination effect we assume the activities of the samples and the contaminant are between 1.5 Bq/m^3 to 3 Bq/m^3 . The atmospheric ^{85}Kr activity can be higher occasionally. But for the majority cases the assumption of a maximum activity of 3 Bq/m^3 is reasonable. We calculate the cross-sample contamination effect with a contaminant of 2.5% volume fraction under the fast analysis measurement protocol. The result is depicted in Fig. 4. It can be seen the relative deviation from the true value caused by cross-sample contamination is less than 2.5%, which is smaller than the typical ATTA analysis uncertainty (3%). The measurement protocol therefore is a good balance between analysis precision and speed.

3. Results and discussion

To test the ability to perform fast ^{85}Kr analysis on air samples, we monitored the ^{85}Kr activity in the air in Hefei from December 2018 to August 2020. Both instantaneous samples and weekly average samples were collected during the twenty-month period (see Appendix for details about the air sampling methods). The air samples were then processed

(1–1.5 L STP were used for each sample) in our laboratory with an automated Kr purification system (Dong et al., 2019). The Kr samples were measured with the ATTA apparatus following the fast analysis protocol for air samples. Fig. 5 shows the result. The ^{85}Kr activity in Hefei air is relatively stable with a slight increase over time ($\sim 0.018 \pm 0.011 \text{ Bq/m}^3/\text{year}$). No significant differences were observed between the weekly average samples and the instantaneous samples, reflecting the fact that Hefei is located far away from any ^{85}Kr emission sources and all possible spikes are smoothed out through the atmospheric mixing process. Interestingly the atmospheric ^{85}Kr activity seems to dip down in the summer. This seasonality maybe related to the fact that the ITCZ (intertropical convergence zone) is migrating to the north in summer and the summer East Asian monsoon is dominantly south-westerly winds. Under these conditions the interhemispheric exchange is enhanced and more air is brought to Hefei from the tropical region and southern hemisphere where atmospheric ^{85}Kr activity is lower (Bollhöfer et al., 2014; Ross, 2010).

4. Conclusion

The method demonstrated in this work lays the groundwork for a global atmospheric ^{85}Kr activity monitoring network. Such a network can further support the continuing establishment of a global ^{85}Kr input function and highlight regional differences, which is important for the emerging ^{85}Kr dating application in groundwater studies. For this purpose one to two stations can be set up in each continent except in Europe, where more monitoring stations will be needed to accommodate the large heterogeneities of the atmospheric ^{85}Kr activity. Monthly average sample can be collected and sent in for ^{85}Kr analysis. ^{85}Kr monitoring for verification purposes might also be possible with further developments.

CRediT authorship contribution statement

W.J., G.M.Y. and Z.T.L. conceived the study. S.M.H., W.J., Z.T.L., F. R. and G.M.Y. contributed to the design of the atom trap trace analysis apparatus. C.G. and S.Y.L built the atom trap trace analysis apparatus. L. U.Z. and J.D.F. performed sample purification. C.G., S.Y.L and W.H.W performed laboratory measurements. W.J., G.M.Y., C.G. and W.H.W. analyzed the data. W.J., F.R., G.M.Y. and Z.T.L. wrote the paper with input from all authors. C.G. and S.Y.L contributed equally to this work.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Air sampling method

The weekly average samples were collected with a continuous air integrator (see Fig. A1.). A 4 L gas sampling cylinder is first evacuated by a diaphragm pump to 0.6 kPa before the air sampling starts. The air then flows into the sample bottle. The flow rate (~ 0.3 mL STP/min) is controlled through a mass flow controller, which ensures a constant flow throughout the whole week. At the end of the sampling period (1-week) there is about 3 L STP air collected in the 4 L sample bottle.

For instantaneous samples, a sample bottle is evacuated with a vacuum pump (to less than 1 mbar) before sampling. The valve of the sample bottle is then opened to allow the air to fill the bottle. The sampling time usually is less than a few minutes.

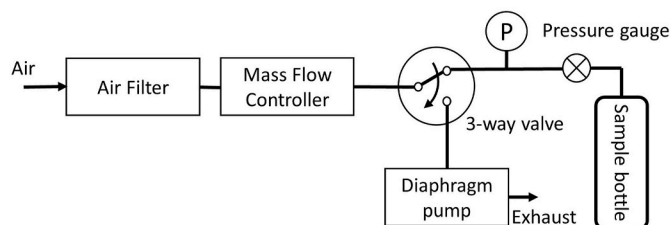


Fig. A1. Schematic of the continuous air sampling device.

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