Upgrade and Further Development of SAUNA Field Report on work task 3.4.7

Replace Carrier Gas

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Sammanfattning

Rapporten innehåller experiment och resultat för vidareutveckling av gasprocessen för SAUNA Field systemet. Uppgraderingarnas syfte är att förbättra kapaciteten för att processa och analysera prov med hög koldioxidhalt samt att byta bärgas till kväve. Detaljerna för detta uppdrag beskrivs i CTBTO kontraktet nummer 2017-1505 (FOI 2017-1283).

Nyckelord: Radioxenon, SAUNA Field, OSI, ädelgas

Summary

This report covers experiments and results from the further development of the gas process for the SAUNA Field system. The upgrades aim to improve the capacity to process samples with high carbon dioxide concentrations and to replace the carrier gas with nitrogen. This work is described in detail in CTBTO contract number 2017-1505 (FOI 2017-1283).

Keywords: Radioxenon, SAUNA Field, OSI, noble gas

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1. Introduction

The Comprehensive Nuclear-Test-Ban Treaty (CTBT) allows for on-site inspection (OSI) in order to collect data for the sole purpose of clarifying whether a treaty violation has occurred or not and to assist in the identification of a possible violator. During such an inspection a wide range of techniques and equipment for collecting facts are available to the inspection team, among others the collection and analysis of radioactive noble gases from both the atmosphere and sub-surface.

In the past 20 years several different systems have been developed for collecting and analysing radioactive noble gases (primary radioxenon and radioargon), both for the international monitoring system (IMS) and for the OSI regime.

As a capability building and to test the concept of the noble gas collection and analysing capability in field, several noble gas analysing systems were developed (xenon systems according to Terms of References in (RFP 2011-0060/ALIMDJANOVA 2011)). These systems where then tested in the field during the integrated field exercise for the OSI regime in Jordan 2014 (IFE14). One of the systems was SAUNA Field, which was previously known as OSI-SAUNA, but will henceforth be referred to as SAUNA Field (or SAUNA-F).

This project is a continuation of this capability building and examines, based upon lessons learned from the IFE14 and other exercises, what needs to be modified and improved on the radioactive xenon field laboratory systems in order to enhance the performance during an OSI. Both in general, and then specifically for SAUNA Field in accordance to the terms-of-reference of the contract number 2017-1505.

This report covers the experiments performed to replace the carrier gas and increase the capacity to process samples with high levels of carbon dioxide for an upgraded version of the SAUNA Field system and the results from these experiments.

The main purpose of the development undertaken was to improve the CO_2 separation capacity to make the system capable of handling all normally expected concentrations, at least up to 20 %, of CO_2 in subsoil gas. The current method, when experiencing elevated levels of CO_2, has been to use external CO_2 traps (“Scrubbers”), a method that is both cumbersome and labour intensive. The goal has been to improve the system such that the external traps for CO_2 will not be required, without reducing the detection sensitivity or the processing capacity of the system.

2. Experimental

The SAUNA Field laboratory prototype at FOI was used for all tests, except while testing new materials for carbon dioxide removal. It should be noted that this system has a slightly different configuration than the field prototype that was delivered to CTBTO in 2013. The lab prototype has been used extensively in several different development projects, without real optimization of the process. Thus, it has a somewhat lower xenon retrieval yield as compared to the system delivered to CTBTO prior to the IFE14 exercise.

The experimental section can be separated into four different tasks, and are described in the following sections:

2.1 Replacing the traps in the sampling oven (SOV)
2.2 Replacing the carrier gas with nitrogen
2.3 Testing of new materials for CO_2 removal
2.4 Adding a pressure swing adsorption separation step

All sample sizes and xenon volumes are given at standard temperature and pressure (STP), 0°C and 1 atmosphere.

2.1 New Sampling oven traps

The first method tested to improve the CO_2 capacity was to increase the amount of molecular sieve (MS) 4A in the sampling oven (SOV) traps. The traps in the Field-prototype held 1 kg of MS4A and just under 2 kg of activated charcoal (AC). The AC was replaced by 470 g of Ag-ETS-10, a more efficient xenon adsorbent, which opened up space for 5 kg of MS. The decision was to keep the current oven design, including the heating power, and try to maximize the CO_2 separation capacity only by changing the amount of MS. A larger oven would not only require a redesign of the system, it would also have a significantly higher power consumption and an increased cool down time, thus reducing the processing capacity of the system. By adding more material, within the limits of the current oven, the times for heating and cooling are slightly increased.

The size of the Ag-ETS-10 trap was not optimized and could probably be reduced. This could speed up the process since the duration of the transfer of the sample from the Ag-ETS-10 trap is depending on the trap size. In order to do so the CO_2 capacity for Ag-ETS-10 for different trap sizes needs to be studied and that was not performed in this study due to time constraints.

After the installation of the new traps the system process was modified to account for the slower heating of the SOV and the larger sample sizes. These changes were mainly in the timing of the process regarding transfer of the xenon sample from the SOV to the processing oven (POV). The maximal temperature in the SOV was decreased from about 300 to 250 °C due to material constraints of the Ag-ETS-10. Both the processing and the regeneration times needed to be extended when the temperature was lowered.

Figure 1. The sampling oven with the three new traps installed, the heating element (not shown) is located next to the wall at the bottom of the picture. The two larger traps are filled with MS4A and the smaller trap, in the centre is filled with Ag-ETS-10.

The large traps could barely fit into the oven, as can be seen in figure 1, and in an industrial design they would likely need to be smaller to be able to install the gas lines. The time to heat up the traps was increased, taking almost 1.5 times (20 minutes) longer to reach the final temperature, see figure 3.

The capacity of the molecular sieve traps was studied by sampling from a premixed balloon containing 8.6 % CO_2 in normal air and measuring on the gas downstream the MS using a mass spectrometer (QMS). The result, see figure 2, shows that the CO_2 breaks through, *i.e.* detected at a 5 % level of the maximal concentration, after collecting 1800 litres. A curve, a Richards equation fitted to the experimental data, and the collected volume at the time for breakthrough are calculated. In these experiments, the fitting function is chosen because it best represents the data and the 5 % level is measurable and reproducible. The interpretation of this is that the system with this design would be able to handle samples, with a volume of two standard cubic metres (SCM), containing up to 8-9 % CO_2.

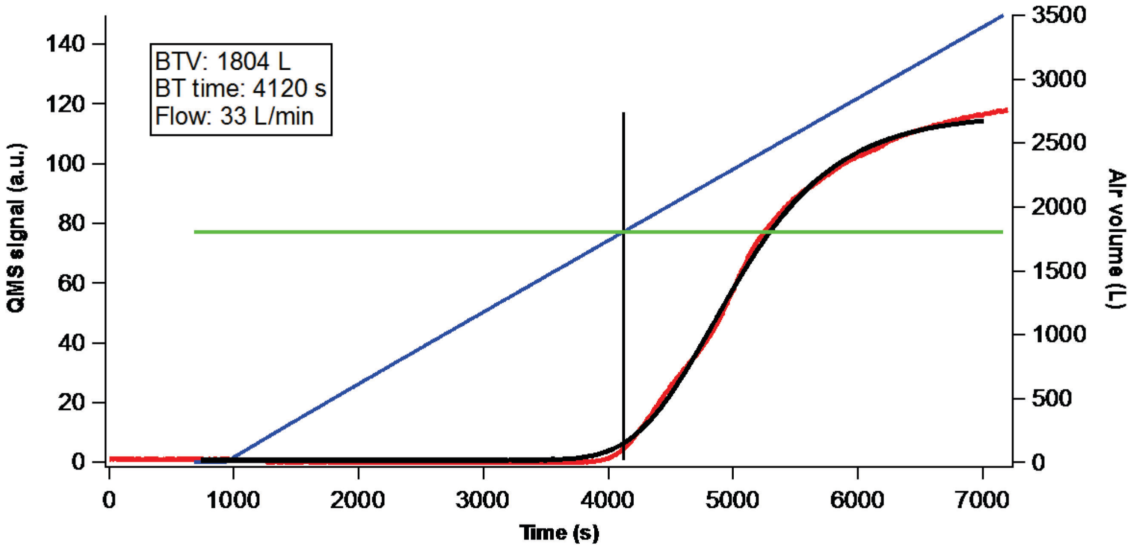

Figure 2. CO_2 breakthrough measurement. QMS signal is shown in red, Richards equation fitted to the data in black and the integrated collected air volume in blue (right axis). The horizontal and vertical lines are guides for the eye.

The CO_2 capacity of the system was also checked by sampling from another premixed sample (2.6 SCM) with an elevated CO_2 content of 9.8 %. The processing of this larger sample showed an impaired process with an early xenon peak in the gas chromatograph (GC) spectrum and a xenon yield that dropped to 55 %, see table 1. This behaviour was also seen during the development of the original system (Aldener, Axelsson, et al. 2014) when processing samples with large CO_2 concentrations.

The conclusion is that 9.8 % of CO_2 is above what the system can process, in this configuration, since this large drop in yield would lower the sensitivity too much to be acceptable for the final system. This carbon dioxide capacity was not deemed sufficient, since the goal is to be able to process samples containing up to 20 %, to be able to get rid of external scrubbers to remove excess CO_2. This together with the slower process, resulting in a lower processing capacity (number of samples/24 h), resulted in an unsatisfactory capacity of the system and the development of an external continuous CO_2 filter which can be integrated into the system, see section 2.4.

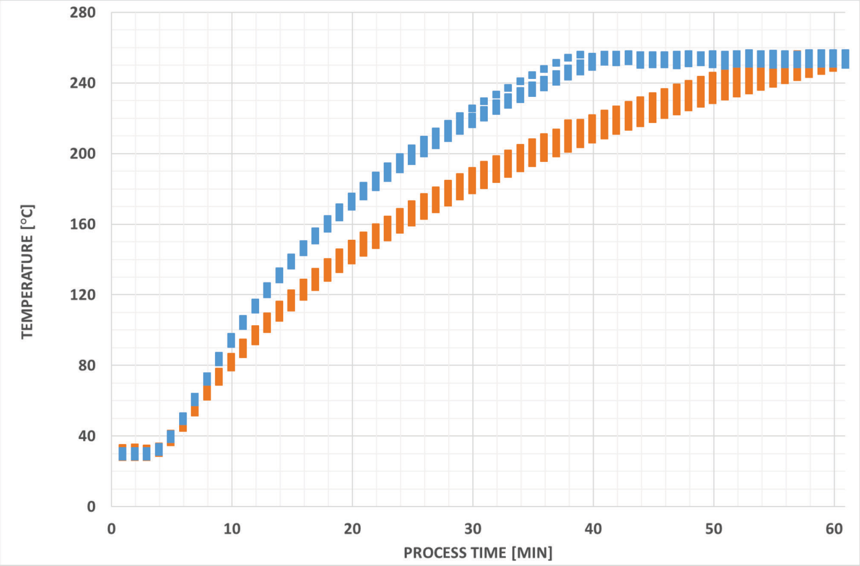

Figure 3. Heating curves with one (blue) or two (orange) MS traps installed in the sampling oven. The curve with only one MS trap installed reaches the final temperature after about 38 minutes.

2.2 Nitrogen as a carrier gas

The gas consumption when regenerating the SOV MS traps increased with the installation of the much larger traps. To investigate if the gas consumption could be reduced as well as removing the high cost and availability problem of helium, nitrogen was tested as a carrier gas. Nitrogen has the advantage of lowering the operating cost and possibly regenerate the traps more efficiently, as compared to helium, but has drawbacks in the gas process and in the detectors. The use of nitrogen instead of helium decreases the resolution of the beta detectors, but this can be compensated for by reducing the pressure in the detector cell. Since the new SAUNA Field design includes larger volume detector cells, developed for SAUNA III, a lower cell pressure can be used. In addition, these detector cells have the advantage of reducing the detector dead volume up to a factor three thus increasing the amount of xenon present in the active part of the detector.

To make the process work with nitrogen mainly the gas chromatograph (GC) process was altered; the processing temperature in the GC was lowered and the pressure and flow changed. The drawback to these changes are larger fluctuations in the baseline signal of the GC, but without impairing the sensitivity of the quantification of stable xenon. After all changes were made to the system, the GC was fully re-calibrated.

Unfortunately, no measurable improvement in the regeneration of the SOV MS trap was observed when using nitrogen. The regeneration flows were measured and optimized and the resulting nitrogen consumption was logged. The regeneration of the SOV MS trap after collecting a sample containing 19 % CO_2 followed by four air samples of various volumes is presented in figure 4. It can be seen that although the carbon dioxide is removed substantially during the first regeneration, parts of it remains in sample number two. It should be noted that the volumes of the third and fourth samples are larger, 9 m^3 and 5.5 m^3 respectively, so they contain more CO_2 than the second and the fifth sample which both have a volume of less than 3 m^3.

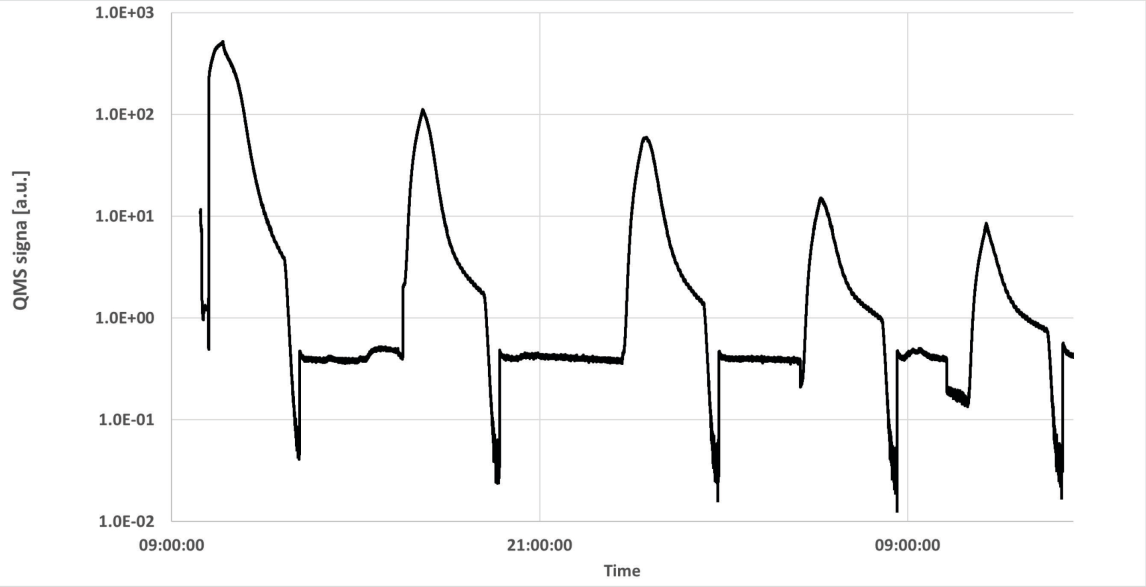

Figure 4. Regeneration of MS4A trap in the SOV, CO_2 measured in drain during regeneration. See text for details.

2.3 Testing new adsorbents

The adsorbing capacity of a few selected materials from ACS materials (ZSM-5, Molecular Sieve Carbon Dioxide Adsorbents Type A and SAPO-34) were tested to see if they could replace MS4A as carbon dioxide remover. Although they all showed good capacity for CO_2 adsorption, all of the materials also adsorbed xenon and could therefore not be used for this application.

2.4 Pressure swing adsorption module

After realizing that the direct adsorption on MS4A was not sufficient, and without finding another suitable material, a different approach was taken. A pressure swing adsorption (PSA) module was added and tested. The PSA technique, in a very similar configuration, has been a part of recent development at FOI for both the SAUNA III and the Cube systems. The advantages of a PSA system is the achievable short cycle time (fast response of the system) in combination with the built-in ability to regenerate the adsorbent while simultaneously sampling, making it a continuously running system. The PSA system that was tested consists of two MS traps, where one is collecting CO_2 at a high pressure while the other trap is being regenerated at a low pressure using the process gas that is exiting the SOV. After a set amount of time, the PSA cycle time, the flow is swapped to regenerate the full trap and instead use the regenerated trap for CO_2 adsorption.

This new module was connected, externally to the prototype at FOI, between the sampling pumps and the SOV. The PSA module is designed in such a way that it can be integrated inside the frame of the SAUNA Field as presented in report 3 (Aldener och Fritioff, Upgrade and Further Development of SAUNA Field Report 3 - Prototype design 2018).

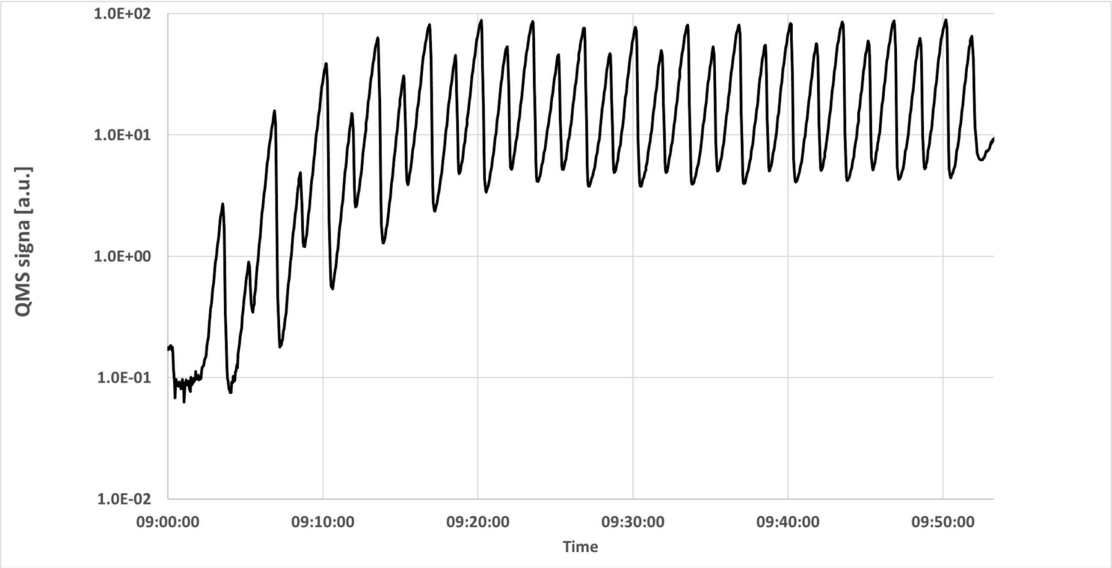

Figure 5. CO_2 measured by QMS out from PSA, note the build-up to a steady-state condition. CO_2 concentration in the sample was 19 %. Measured in the flow collected in the SOV.

Several different trap sizes and timings of the PSA system were tested, see table 1. Only MS4A was used in these traps. Several air samples were collected in order to characterize the system and to measure the system's capacity for ambient air samples. For the tests with elevated CO_2 and CH_4 levels, *i.e.* simulated subsoil samples, only samples of about 2 m^3 were considered, see table 1 and table 2. These tests were performed by adding either pure CO_2 or CH_4, or a mix thereof, to either a balloon or a pressurized container (SCUBA bottle) and then filling up with ambient air. The samples were then collected and processed, and the resulting xenon retrieval yields were obtained. The process was studied, with mass spectroscopic measurement, to verify the regeneration of the different traps and to observe when, and if, CO_2 and xenon breakthrough occurs. An example of this is seen in figure 5 where the CO_2 is measured downstream of the PSA while sampling a CO_2 enriched sample. The integrated CO_2 concentration, collected in the SOV, is much lower than in the sample and strongly depends on the sample concentration in a non-linear fashion. The PSA reaches a threshold, around 20 %, when the CO_2 capacity is only depending on the SOV MS trap capacity. The oscillation is from the cyclic process of the PSA and shows the CO_2 as it breaks through in the two different traps. The asymmetry is due to difference in flow through the two traps in the first prototype.

Table 1. CO_2 tests using the PSA module.

PSA timing (s)	MS4A in each PSA trap (g)	CO_2 concentration in sample (%)	Sample size (SCM)(*)	Xenon retrieval yield (%)(**)
400	2800	10.4	2.0	73.3
400	2800	18.2	2.1	74.6
300-400	1700	16.0	1.5(+5 m^3 air)	77.3
200-300	1700	24.0	2.3(+6 m^3 air)	73.7
200	1700	18.5	2.0	77.8
50	870	24.5	2.2	72.7
100	1700	20.3	2.5	80.4
100	1700	19.5	2.5	79.9
100	1700	24.6	2.4	82.0
100	1700	19.1	2.5	80.8
100	1700	35.2	2.5	58.6
100	1700	29.2	2.7	53.4(***)
100	1700	21.5	2.5	77.6(***)

(*) Corrected for flowmeters response to CO_2.

(**) Corrected to expected amount of xenon in sample air, *i.e.* CO_2 volume subtracted. The uncertainty in the yield is about 5% (k=1).

(***) Pressurized samples

Table 2. Methane measurements.

PSA timing (s)	MS4A in each PSA trap (g)	CH_2 concentration in sample (%)	Sample size (SCM)	Xenon retrieval yield (%)
100	1700	0.39	2.4	85.3
100	1700	0.20	2.4	85.5
100	1700	0.2 plus 22% CO_2	2.5(*)	83.5(**)

(*) Corrected for flowmeters response to CO_2.

(**) Corrected to expected amount of xenon in sample air, *i.e.* CO_2 volume subtracted.

3. Results

The SAUNA Field system was tested with a pressure swing adsorption (PSA) module to increase the capacity to process samples with high CO_2 concentrations, eliminating the need for external CO_2 scrubbers. The traps in the sampling oven has also been replaced, to make room for more MS4A a more efficient adsorbent, Ag-ETS-10, has replaced the original activated charcoal. This resulted in a xenon retrieval yield of 76±5 %, for a 2 SCM sample with a CO_2 concentration below 20 %. Note that this yield is for the first SAUNA Field laboratory prototype, and will most likely be higher for a newly built system. Prior to these tests the yield was about 90 %, for a 2 SCM sample with a CO_2 concentration below 2 %.

The lower dead volume in the new detector cells will compensate the somewhat lower yield, and no significant change in sensitivity is to be expected in the final system. The system capacity for ambient air samples, i.e. samples with low CO_2 concentration, has increased from 2-3 to 12 SCM, see figure 6, without experiencing a significant drop in yield. Due to these changes, the system has a slightly longer processing time reducing the number of samples that can be processed every 24 hours from 6 to 4.5. The PSA module does not affect the processing time, the slower process is due to the changes to the traps in the sampling oven.

The additional PSA unit can be added to the system after the system is built.

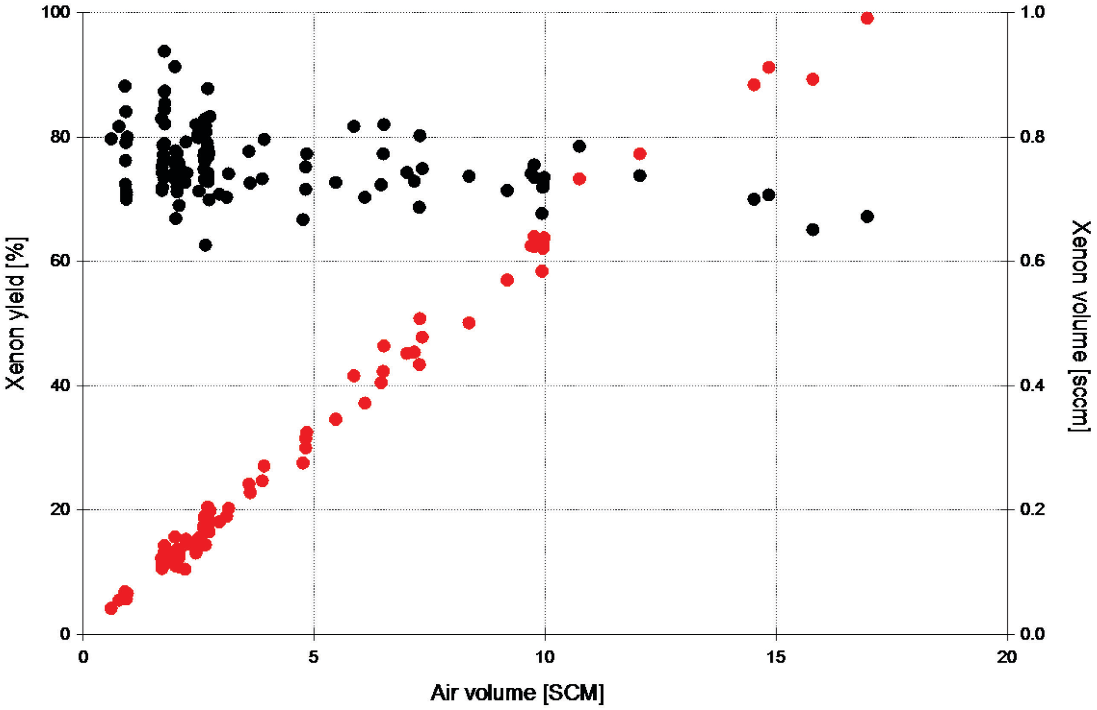

Figure 6. Xenon volume (red on right axis) and xenon retrieval yield (black on left axis) for the system in the new configuration, with PSA and Ag-ETS-10 trap, as a function of sample size when collecting ambient air.

4. Conclusions and outlook

Different methods were tested with the aim to increase the capacity of the SAUNA Field system to process samples with elevated CO_2 levels, which can be experienced in subsoil gas. It was found that the most promising method was to add a PSA unit before the sampling oven. This allows processing of samples with a very high carbon dioxide concentration without using external scrubbers. The PSA module is both simple in its design and easy to operate. CO_2 in subsoil gas can reach very high levels but an estimate is that a capacity of 20 %, for a 2 m^3 sample, will work for most areas around the globe. For more extreme conditions, it will be necessary to reduce the sample size or expect a lower xenon yield. This new PSA module can be integrated into the existing frame of the new design for the SAUNA Field system.

The helium carrier gas was replaced with nitrogen, this will lower the operating costs as well as improve the logistics since nitrogen is usually more readily available around the world. Using a nitrogen generator instead of pressurized bottles could potentially work but has not been investigated so far. Caution has to be made for each specific nitrogen generator since it produces fresh nitrogen from the ambient air that potentially contains trace amounts of radioactive xenon that could contaminate the process.

Although the final solution, with the PSA and larger MS4A traps, reduces the xenon retrieval yield and the capacity of the system, it was nonetheless found to be the best solution due to its simplicity, level of automation, and a very high CO_2 capacity.

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