Procedure for Xe purity calibration

Purpose: for a meaningful measurement, we need to know the ratio between the true molar ratio in the sample and the Kr to Xe molar ratio measured by the RGA. This ratio of ratios is the calibration constant of the system.

All values not automatically recorded in data files and every special occurrence need to be saved in an excel workbook (the measuana.xlsx contains template spreadsheets, and can be used as model). The RGA data must be saved in ASCII format, and snapshots of the RGA plots should be pasted in the excel spreadsheet of the measurements.

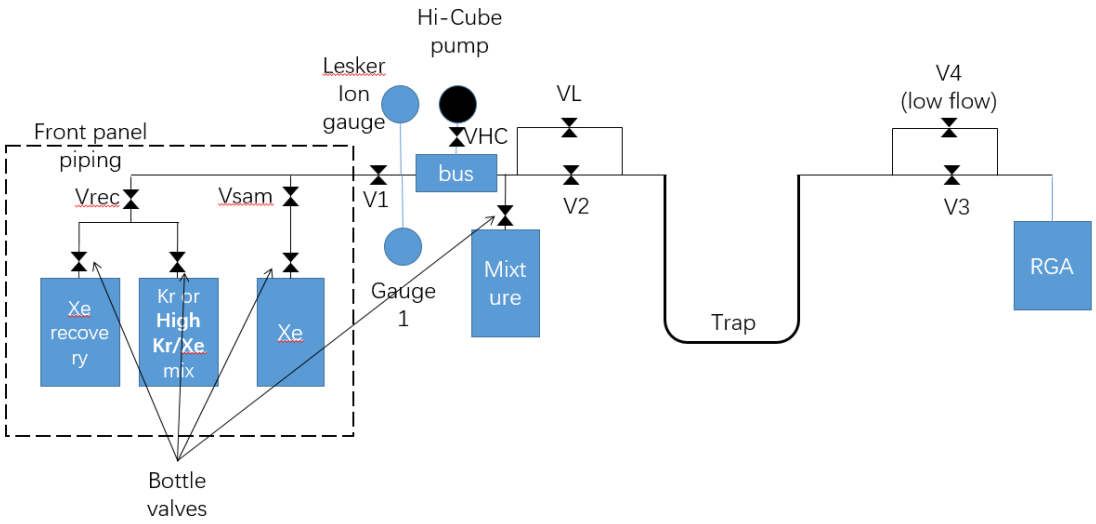

Fig. 1 Schema of the Xe purity system. V1 closes the connection between the front piping and the bus. Vsam is the sampling valve, ***not to be confused*** with the *sample bottle valve*., while Vrec is the valve shutting the path from either the recovery or the calibration bottle to the bus.

This procedure is a *variant* of the procedure in (1), so you should *read that first*.
The valve nomenclature used below is displayed in Fig. 1. For the physical locations, you can refer to Fig.s 3-5 of Ref (1). V1 is usually left open, unless it is necessary to completely isolate the main system from the front piping. If V1 is closed, you won't be able to inject gas into the system. Vsam is the sampling valve, ***not to be confused*** with the *sample bottle valve*. Fig 1 should make this clear. Valves on the bottles do not have specific names.
The summarized procedure is:

1) Make a mixture with accurately known Kr molar fraction.
2) Perform a measurement of this mixture following Ref. (1).
3) Calculate the ratio of the partial pressures of ^{84}Kr and ^{132}Xe as measured by the RGA then divide by the isotopic abundance of ^{84}Kr in Kr, and multiply by the isotopic abundance of ^{132}Xe in Xe.
4) Divide the known molar fraction of Kr in the calibration sample by the ratio calculated in 3). The result, C, is your calibration: when you perform a measurement of a regular sample,

the true Kr concentration is C x P_{Kr}/P_{Xe}, with P_{Kr} and P_{Xe} as measured by the RGA.

The detailed procedure for 2) is in a separate document, while 3) and 4) are self-explanatory, so here only 1) will be detailed.

The initial state of the system, and consequently the initial checks and correction of anomalous state are the same as in the normal measurement procedure (1). We'll copy them here for simplicity:

1. Initially the system should be under high vacuum, so check the various gauge pressures. The front panel has several displays, shown in the left Fig. 2 of Ref (1). The normal pressures displayed in the vacuum state are clearly visible. If any of these pressures is significantly higher, find out why. If a filled bottle has its valve not fully closed, you probably lost a large fraction of its content. Other 2 pressures to check are behind the front panel, on the Lesker ion gauge (see Fig. 2 of (1), right side), and on the red HiCube pumping station. If the station's display shows something else (e.g., the rotation speed), browse through the parameters until you find the pressure. Note that the unit on the pump display is hPa, not Pa. The Lesker gauge and the pump should read similar pressures (within a factor of 2, after conversion to the same unit). ***Most important pressures***: ion gauge of RGA side $\leq$ 1e-5 Pa, pump (bus side) and Lesker ion gauge $\leq$ 2e-4 Pa.
2. Check the configuration: the valve of the HiCube pump (VHC in the schema of Fig. 1) and valves Vsam, Vrec, V1, V3 and V4 should be open, while V2 and VL (leak vale) should be closed, and the RGA off. The valves of any bottle that shouldn't be empty should be closed. If not, you have likely lost the bottle's content. *Note*: if Vsam was not open, you likely have air between the sample bottle valve and Vsam (in the elbow at the right of Vsam, see Fig. 3 of Ref. (1)). In this case:
    a) Turn off the lesker, the RGA ion gauge and the HiCube's turbo component (wait that the turbo's rotation speed is zero)
    b) Slowly but fully open Vsam
    c) Turn the HiCube's turbo on and wait that the Pirani, Gauge 1, Gauge 2 and the HiCube return to the normal readings. Then turn the Lesker and the RGA ion gauge on and check that everything is back to normal.
3. Connect a pure Kr bottle to one of the normally free swagelok connectors on the Vrec side of the front panel (see Fig. 2) and a sample bottle containing Xe with impurity concentration known to be at least 10x lower than the mixture you want to make.
4. Close or make sure that the valves Vsam, Vrec, V2, and VL are closed. Also make sure that the recovery bottle valve (not shown) is closed. This procedure does not use the RGA, so, as long as you keep V2, and VL fully closed, V3 and V4 should remain fully open to continue the vacuum purging of the RGA side. Turn the ***Lesker*** gauge ***off*** and close its valve.
5. Check the records on the mixture bottle (the only bottle not hanging from the front panel), and its valve:
    a) if it is recorded as filled with a known mixture and the valve is closed, then it is a calibration bottle. If the composition is already what you want you don't need to make a new mixture, Just move this bottle to the front panel (see Fig. 2 for position). Otherwise

replace the mixture bottle with an empty one. As “empty” really means “filled with air”, proceed as in b).

b) if the valve is closed and you are sure that the content is air, check that V2 and VL are closed and ***turn off*** the turbo component of the HiCube pump. When the HiCube rotation speed is back to zero, slowly but fully open the mixture bottle’s valve. Restart the HiCube to restore the vacuum in the bus and make vacuum in the bottle.

c) if the valve is closed but the content is unknown, it probably contains some Xe, so transfer its content to the recovery bottle. To do this, check that V2 and VL are closed and close VHC. ***After*** closing VHC, ***turn off*** the turbo component of the HiCube pump. Cool down the recovery bottle by submersion in LN. Close Vrec, open the recovery bottle valve and monitor the pressure of G2. When G2 reads the lowest pressure, the recovery bottle is frozen. At this point, first open Vrec, then the mixture bottle valve. When the pressures of G1 and G2 are both minimum, close the recovery bottle valve, check that the speed of the HiCube is zero, then open VHC and restart the HiCube to reestablish the vacuum in both the bus and the mixture bottle.

d) if the valve is open, it means that in the last measurement the bus volume was augmented by this bottle’s volume, and the trap inflow rate was measured wrongly. So the last measurement should be repeated or reanalyzed, but the mixture bottle is empty and under vacuum, so it’s ready to make a calibration mix.

6. Once you have the mixture bottle open to the bus and at its normal vacuum pressure (order of 1e-4 Pa or lower. If you read the pressure from the HiCube pump, remember that its unit is hPa, so it should read ~1e-6 or less), the system is ready for mixing. The initial state should be: V2 and VL closed, Vrec, V1, VHC and Vsam open. The mixture valve should also be open. Turn ***off*** the Lesker ion gauge and close its valve, close Vsam and VHC, then turn off the turbo of the HiCube.
7. Transfer 0.2 bar[1] (as read from G1) of Kr to the bus, the most reliable way is to use a regulator to control the outflow from the Kr bottle, then ***close*** the Kr bottle and the ***mixture bottle*** valves. Make sure the HiCube speed is zero, then open VHC and Vsam, and restart the HiCube turbo. Also open the Lesker valve, but leave this gauge ***off***.
8. When the vacuum of G1 and G2 are both minimum, and the HiCube reads a pressure of order 1e-6 hPa, turn the Lesker on and check that also its reading is ~1e-4 Pa or less.
9. When the Lesker reads 1e-4 Pa or less, turn it ***off***, close its valve and VHC. Turn off the HiCube turbo. Close Vrec, then transfer 5 bar of pure Xe from the sample bottle to the bus.
10. Close the mixture bottle valve. Now the mixture bottle contains ~4% Kr in Xe (exact value in Table 1).
11. Replace the mixture bottle with an empty bottle. This is your new mixture bottle, while the old one is now a calibration bottle. Connect the latter to the front panel, in the place shown in Fig. 2.
12. Record the current Kr content of the calibration bottle.
13. Recover the content of the bus to the recovery bottle:

[1] At this stage, the Pirani gauge is not correctly calibrated, and the minimum reliable pressure reading of G1 from specs is 2% of its 10 bar full scale. If the electronic noise is below 5 mV, we can push to 25 mbar, but a calibration mixture needs to have top reliability.

a) Cool down the recovery bottle by submersion in LN.
b) Close Vrec, open the recovery bottle valve and monitor the pressure of G2. When G2 reads the lowest pressure, the recovery bottle is frozen.
c) Open Vrec.
d) When the pressures of G1 and G2 are both minimum, close the recovery bottle valve and open the new (air-filled) mixture bottle, check that the speed of the HiCube is zero, then open VHC and restart the HiCube to reestablish the vacuum in both the bus, the new mixture bottle and the front panel piping.

Now, there are two options: one is to make a series of bottles with known but decreasing Kr content, each containing 5 bar. As seen from Table 1, this requires a lot of them. Therefore, this procedure continues with the alternative of reusing the same bottles and dumping the excess mixtures to a big recovery bottle. The latter could be run through the Kr distillation tower to get back high purity Xe.

14. After the previous step, the system should be in the following configuration: V2 and VL closed. VHC, V1, Vrec and Vsam open. Lesker valve open but Lesker gauge ***off***. Bottles closed, except for the new mixture bottle. Check that this is the configuration, and that the vacuum is good. Use the Lesker gauge after the HiCube shows a pressure less than half the Lesker's maximum operating pressure.
15. Repeat this procedure from step 4 to step 7, both included.
16. Dump the residual content of the calibration bottle to a large recovery bottle (e.g., a 50 liter bottle capable of holding 150-200 bar). This way the calibration bottle will become the new mixture bottle.
17. Follow steps 8 through 13, both included (of course, the "new mixture bottle" of step 11 is the old calibration bottle of step 16). At the end of each of these iterations you should have the corresponding Kr fraction in Table 1.
18. Repeat step 14 through 17 until you reach the target level of Kr. Whenever the Xe sample bottle runs low on Xe, refill it with the same purity Xe.

Table 1: number of iterations needed to achieve various levels of Kr. The 0-th iteration is, of course, the pure Kr bottle, normally with 10 ppm total impurities. If your target Kr content is, e.g., ~10 ppb, make sure your Xe impurity is 1 ppb or better

iteration	Kr fract (ppm)
0	999990
1	39999.6
2	1599.984
3	63.99936
4	2.5599744
5	0.102398976
6	0.004095959
7	0.000163838
8	6.55353E-06
9	2.62141E-07
10	1.04857E-08

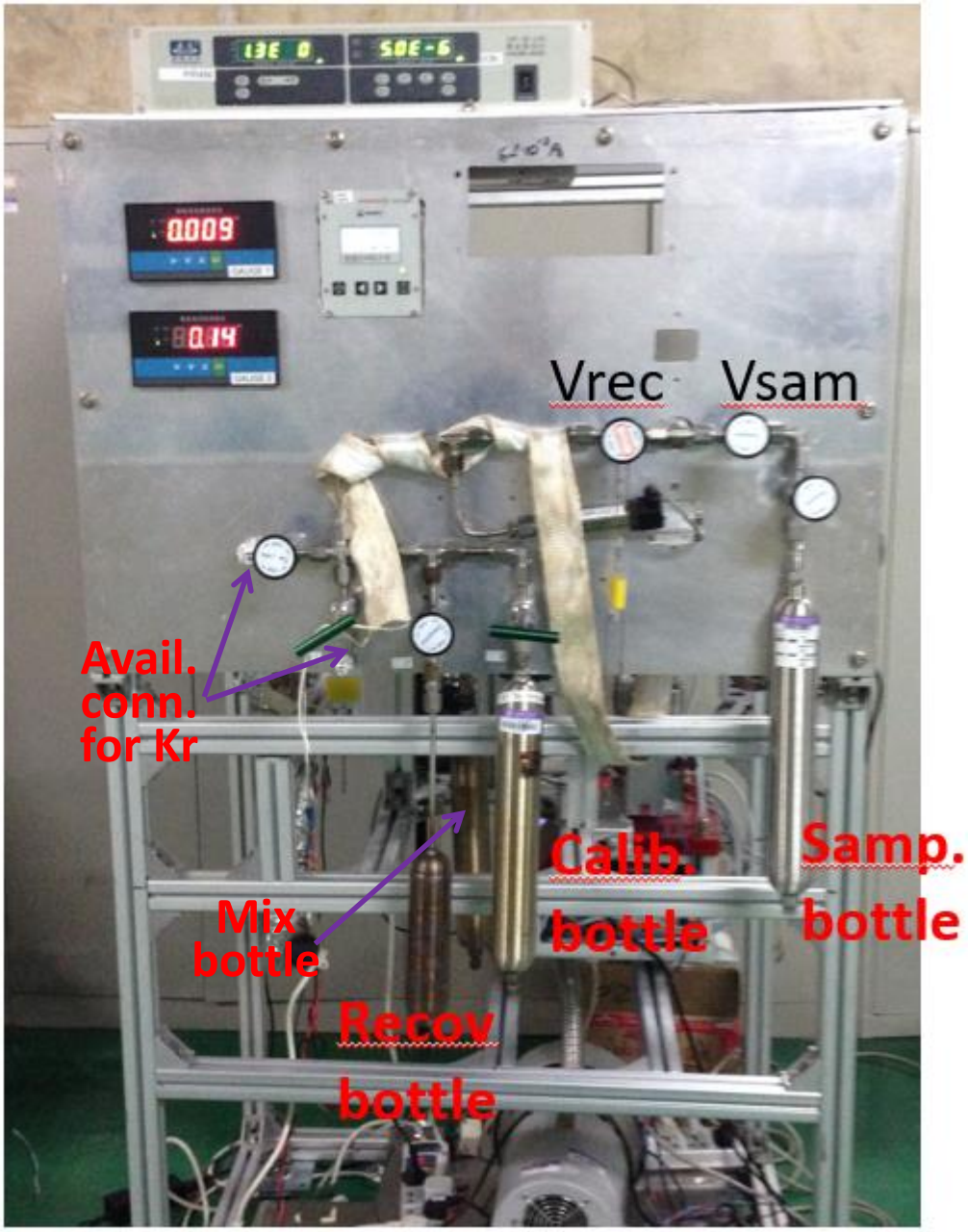

Fig. 2 Front panel with marked bottles and available hook-ups for the Kr bottle

Bibliography

1. **Procedure for Xe purity measurement with continuous flow.**