Application Bulletin

Of interest to:	General analytical chemistry, comparison, sampling systems, overflow pipette, dosino loop, loop sampling, LSS, DSS, OFP	P 1

Comparison of different sampling systems for ProcessLab

Introduction

Every analytical system contains techniques and devices for integrating and performing different tasks such as analyses, calculations, transferring of liquids, data processing, etc. Reproducible sample metering is an often underestimated task that has a direct effect on the accuracy of the result. Appropriate equipment is therefore of the utmost importance.

There are three different sampling systems available for ProcessLab. In this Application Bulletin you will find a detailed description of the various systems, their use and typical areas of application. This bulletin also includes a comparison of the sampling systems and some practical results obtained with the various approaches.

Sampling systems

Loop sampling system – LSS

The loop sampling system for ProcessLab consists of a sample loop between two 3-port valves. In one valve position the loop is flushed and filled with the sample. After flushing with sample the valve is switched and the sample transferred to the vessel using a transfer reagent (in most cases demin. water). Sample loops are available in 1, 2 and 5 mL versions.

Dosino sampling system – DSS

The Dosino sampling system is made up of a tubing of 150 cm length which is connected to port 1 of a Dosino with 20 mL buret. This combination allows to take variable sample volumes from 1…10 mL directly from the titration vessel. The sample remains in the tubing, locked-in between two air bubbles, until it is released into the measuring cell.

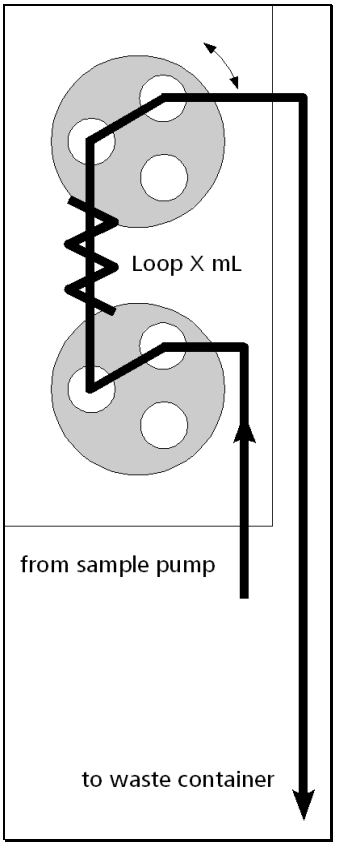
Overflow pipette – OFP

The overflow pipette is a glass cylinder which is filled filled with sample from below. When the pipette is full and has been overflowing for a certain time a valve is switched and the sample released into the titration vessel. Sampling with the overflow pipette is fast and reproducible.

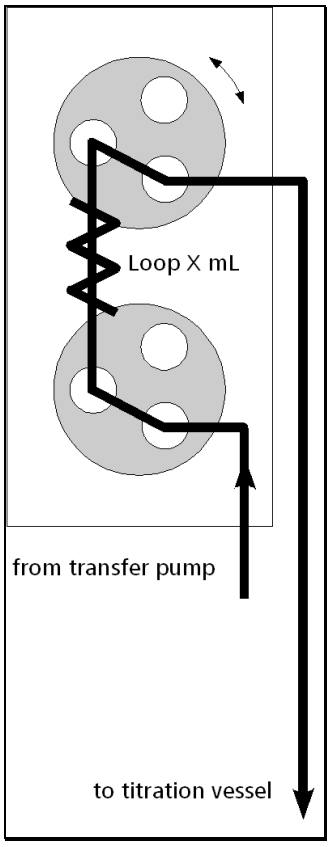
Description of sampling systems

Loop sampling system – LSS

The loop sampling system consists of two valves which are switched by ***tiamo*** between sampling and transfer position. The loop is a normal FEP tubing (1, 2 or 5 mL) which is connected to both valves.



Schematic of loop valves in sampling position (Valve "OFF")



Schematic of loop valves in transfer position (Valve "ON")

Please note that any loop needs to be calibrated before being used for the first time. This should be carried out with an appropriate titration and subsequent calculation. The exact volume is saved as a common variable in ***tiamo***. Recalibration should be done on a regular basis, for example monthly.

Dosino sampling system – DSS

This sampling needs a Dosino and a tubing of appr. 150 cm length which has a total volume of slightly more than 10 mL. The sample volume is variable (1…10 mL)and sampling can be repeated within the same method with full volume flexibility and with the Dosino's reproducibility.

Contamination of the Dosino or diffusion cannot occur due to the strict separation between sample and demineralized water. When the sample is released the loop is flushed with water which is already in the Dosino. This is to make sure that the complete sample has been collected and transferred to the titration vessel. Depending on the sample it might be necessary to flush the Dosino loop with a higher amount of flushing solution.

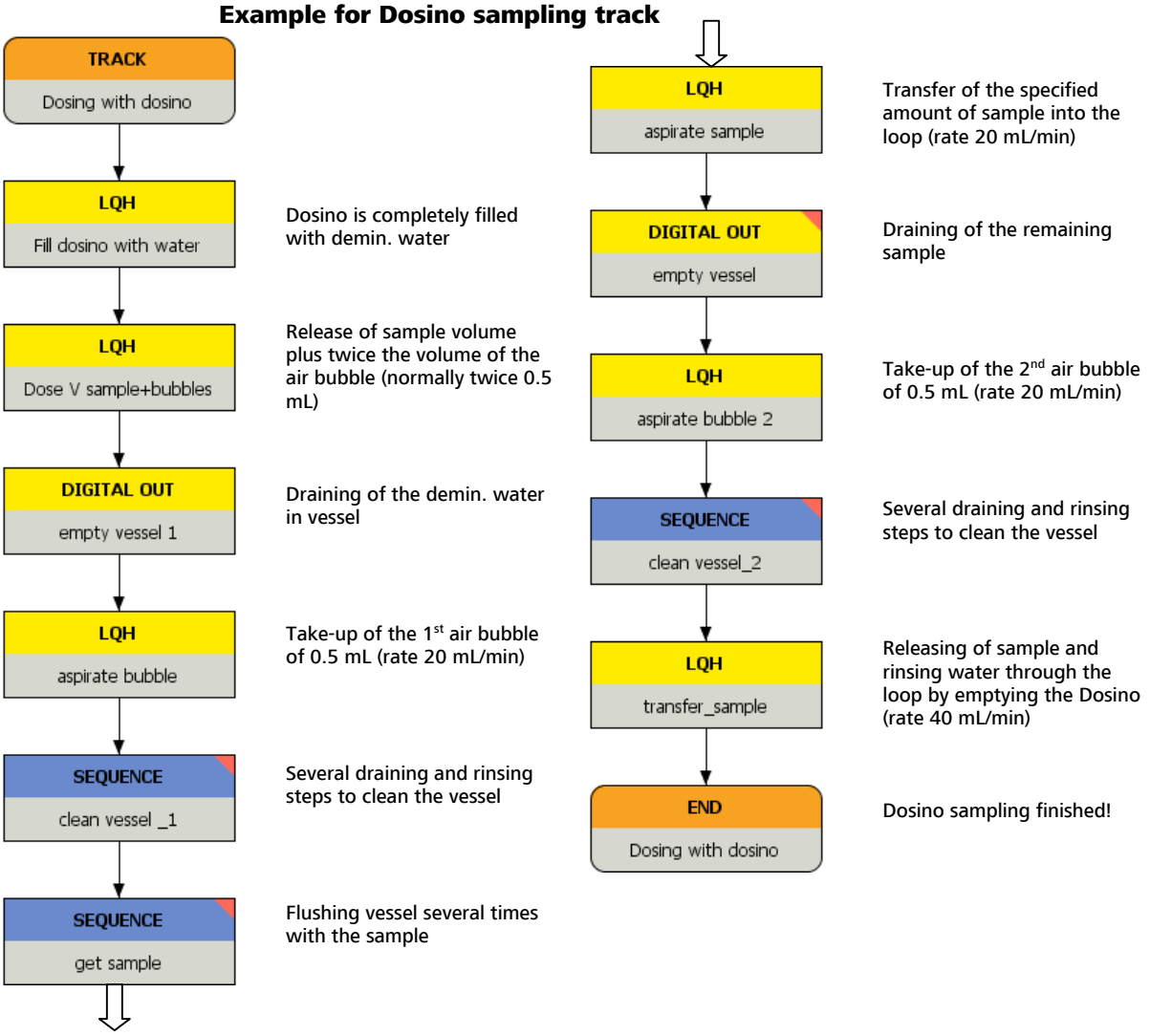
The following procedure describes the steps which are necessary to measure a sample with the Dosino sampling system.

Procedure

The general procedure can be divided into the following steps:

- Sample transfer to the vessel
- Transfer of sample volume into loop
- Cleaning vessel
- Releasing sample from loop into vessel

Example for Dosino sampling track



Overflow pipette sampling system - OFP

This way of sampling is very fast and accurate and uses the hydrostatic pressure (gravity force). The overflow pipette consists of a cylindrical glass which is filled from below. The upper round-shaped part has two tubing connections, one for the waste (overflowing sample) and the other one for pressure compensation. To switch between fill and release a solenoid valve is needed. ***tiamo*** is used to switch the valves "ON" or "OFF". Please see Application Bulletin 296 for further details about the solenoid valve module and the valves.

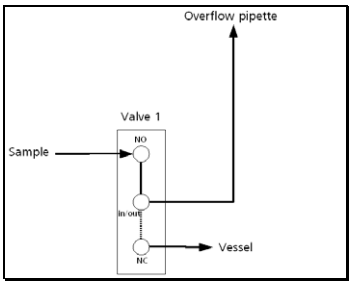
Prior to the first determination the overflow pipette needs to be calibrated and the volume saved as a common variable. Cleaning and rinsing is not necessary as the pipette is always flushed with sufficient sample.

Considerations

- Valve switching times should be evaluated prior to the first measurement and saved as a common variable (fill time & release time). A regular check with a standard solution is recommended (possibly also a recalibration).
- Changes of tubing or the overflow pipette require a recalibration
- The overflow and pressure compensation tubing should always go downwards and not dip into the liquid waste
- The effective sampled volume consists of the content of the overflow pipette plus the liquid in the tubing ($V_{effective} > V_{nominal}$)

In principle there are two slightly different ways of using the overflow pipette. In both cases a solenoid valve module is needed.

Using only one valve (filling or releasing)



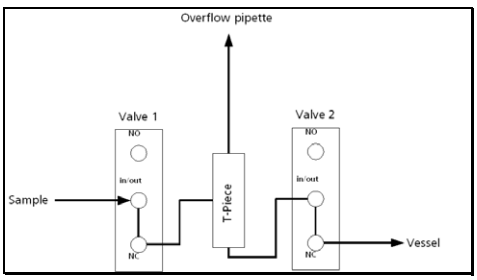
Functions

Filling/overflow
Valve 1 OFF

Release sample
Valve 1 ON

This easy and very rapid method allows very rapid sampling. The only difference between filling and transferring is the position of the valve. When it is switched "ON" the sample immediately flows to the titration vessel. In the "OFF" position the overflow pipette is flushed with sample.

Using two valves (filling, waiting and releasing)



Functions

Filling/overflow
Valve 1 ON
Valve 2 OFF

Release sample
Valve 1 OFF
Valve 2 ON

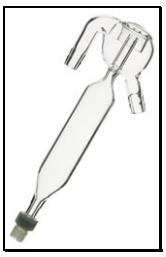
Waiting
Valve 1 OFF
Valve 2 OFF

This method is used if varying waiting times have to be inserted between sampling and sample transfer to the vessel. In some cases it is also necessary to let the sample settle for some time (e.g. viscous samples).

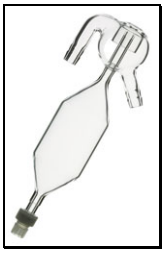
Spare parts for overflow pipette

6.7206.300; 6 mL overflow pipette (incl. M8 connector)

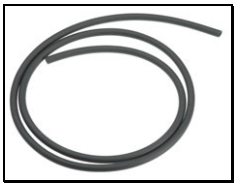
6.7206.310; 10 mL overflow pipette (incl. M8 connector)



6.7206.320; 20 mL overflow pipette (incl. M8 connector)



6.7206.330; 50 mL overflow pipette (incl. M8 connector)



6.7205.150; Norprene tubing d=6.4 mm, L=2 m (one tubing)

6.1811.010; adapter M8/glass connection

Metrohm ProcessLab

No. 290e

Sampling systems overview

	Loop sampling system - LSS	Dosino sampling system - DSS	Overflow pipette - OP
Sample size	Fixed	Variable	Fixed
Sample size (volume)	1, 2 or 5 mL	1 - 10 mL	6, 10, 20 or 50 mL
Preferred for ...	Agressive samples which should be diluted before getting in contact with the electrode	Samples containing solids or air bubbles	Agressive samples which may contain bubbles but no solids
Not recommended for ...	Samples containing solids or air bubbles Saturated solutions	Samples which might damage the electrode	Viscous or saturated samples
Advantages	Very fast sampling Parallel tasking possible (e.g. vessel cleaning) Sample can be flushed with reagent	Var. volume (diff. volumes in a single method) High flexibility No calibration needed	Fast sampling Needs very little space Parallel tasking possible (e.g. vessel cleaning)
Disadvantages	Fixed volume Max. pump speed 40 mL/min Periodical calibration	Requires several rinsing steps Electrode gets in contact with sample	Fixed volume Sensitive glass part Periodical calibration
Ordering numbers	6.7206.000; loop sampling system 6.1805.080; 1 mL Loop or 6.1805.020; 2 mL Loop or 6.7206.030; 5 mL Loop	6.7203.100; Dosino mounting device 2.800.0010; Dosino 800 6.3032.220; Dosing unit 20 mL 6.7206.040; Sample loop 1-10 mL (mounted)	6.7206.100; 6 mL Pipette, complete 6.7206.110; 10 mL Pipette, complete 6.7206.120; 20 mL Pipette, complete 6.7206.130; 50 mL Pipette, complete
Additionally needed	6.7205.010; Sample pump 40 mL/min 6.7205.010: Transfer pump 40 mL/min 6.7202.500; Relay output (max. 2 LSS)	6.7205.020; Sample pump 120 mL/min	6.7206.210; Solenoid valve module 6.7206.220; Solenoid valve PEEK/FFKM Sample pump 120 mL/min
Spare parts	6.1805.080; 1 mL Loop 6.1805.020; 2 mL Loop 6.7206.030; 5 mL Loop	6.1805.220; Sample loop M8 1-10 mL, loop only	6.7206.300; 6 mL Pipette, spare part 6.7206.310; 10 mL Pipette, spare part 6.7206.320; 20 mL Pipette, spare part 6.7206.330; 50 mL Pipette, spare part 6.1808.060; T-Piece 3x M6

Some calibration examples (NaOH-HCl titration, both 0.1 mol/L)

These results were achieved by a simple titration of a given volume of NaOH. The titrant used was 0.1 mol/L HCl. Sample and titrant are standardized solutions which were bought from a lab chemicals supplier. Therefore the evaluated endpoint volume corresponds directly to the measured sample volume (sample size).

		Loop sampling system*	**Dosino sampling system***		**Overflow pipette****	
	V nominal	5 mL	10 mL	5 mL	6 mL	10 mL
		Volume	**Volume**		**Volume**	
Volume calibration	1.	4.795 mL	9.956 mL	4.984 mL	6.814 mL	10.320 mL
	2.	4.787 mL	9.972 mL	4.990 mL	6.810 mL	10.320 mL
	3.	4.786 mL	9.985 mL	4.984 mL	6.787 mL	10.310 mL
	4.	4.780 mL	9.975 mL	4.973 mL	6.800 mL	10.328 mL
	5.	4.801 mL	9.969 mL	4.977 mL	6.787 mL	10.322 mL
	6.	4.784 mL	9.980 mL	4.984 mL	6.814 mL	10.333 mL
	7.	4.793 mL	9.983 mL	4.975 mL	6.827 mL	10.320 mL
	8.	4.784 mL	9.987 mL	4.982 mL	6.823 mL	10.305 mL
	9.	4.777 mL	9.981 mL	4.976 mL	6.799 mL	10.323 mL
	10.	4.773 mL	9.975 mL	4.984 mL	6.818 mL	10.312 mL
	Sample volume/mean	**4.786 mL**	**9.976 mL**	**4.981 mL**	**6.808 mL**	**10.319 mL**
	s (absolute)	**0.0085 mL**	**0.0092 mL**	**0.0054 mL**	**0.0141 mL**	**0.0084 mL**
	s (relative)	**0.18 %**	**0.09 %**	**0.11 %**	**0.21 %**	**0.08 %**

Method validation	1.	4.794 mL	9.966 mL	4.984 mL	6.812 mL	10.325 mL
	2.	4.797 mL	9.975 mL	4.976 mL	6.806 mL	10.310 mL
	3.	4.782 mL	9.975 mL	4.990 mL	6.802 mL	10.316 mL
	4.	4.804 mL	9.980 mL	4.986 mL	6.780 mL	10.315 mL
	5.	4.802 mL	9.992 mL	4.995 mL	6.820 mL	10.335 mL
	6.	4.796 mL	9.986 mL	4.970 mL	6.814 mL	10.308 mL
	7.	4.792 mL	9.980 mL	4.972 mL	6.826 mL	10.322 mL
	8.	4.774 mL	9.984 mL	4.983 mL	6.810 mL	10.302 mL
	9.	4.777 mL	9.967 mL	4.985 mL	6.808 mL	10.322 mL
	10.	4.792 mL	9.985 mL	4.980 mL	6.812 mL	10.308 mL
	Consumption HCl	**4.791 mL**	**9.979 mL**	**4.982 mL**	**6.809 mL**	**10.316 mL**
	s (absolute)	**0.0102 mL**	**0.0083 mL**	**0.0078 mL**	**0.0123 mL**	**0.0099 mL**
	s (relative)	**0.21 %**	**0.08 %**	**0.16 %**	**0.18 %**	**0.10 %**

Discussion

The sampling method can be chosen based upon the technical needs mentioned in the overview table. The evaluation of the different sampling systems resulted in no significant differences.

These repeatability results (n=10) can be reached under optimized lab conditions. Please be aware that the standard deviations obtained under conditions in a process environment may be higher!

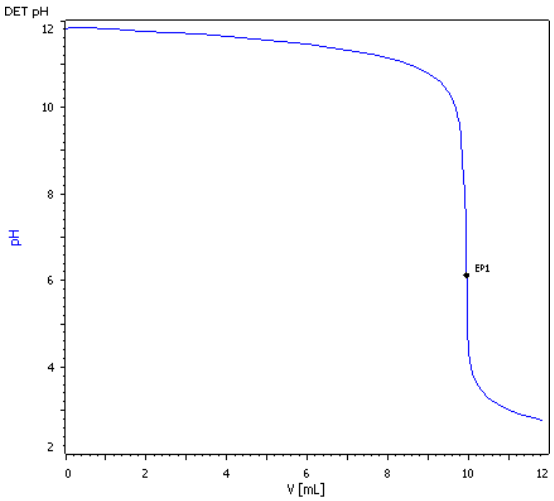
Remarks

*The effective volume slightly differs from the nominal volume because a standard FEP tubing is used for this task.

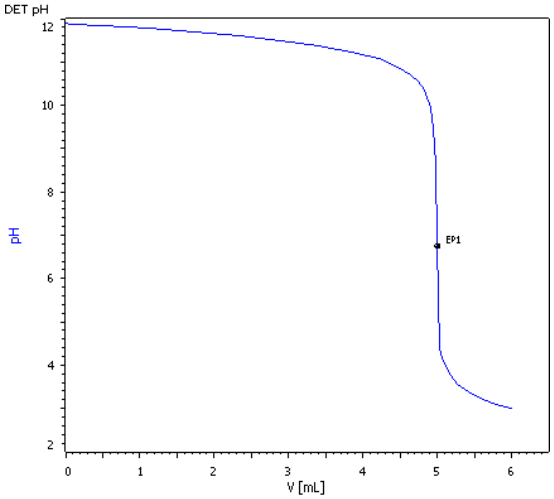
**Due to the hydrostatic pressure and the tubing through which the sample flows from the pipette to the vessel, a certain part of the tubing volume is included in the volume calibration.

Practical examples

Titration curve with the Dosino sampling system, 10 mL
Sample 0.1 mol/L NaOH



Titration curve with the Dosino sampling system, 5 mL
Sample 0.1 mol/L NaOH



Titration curve with the overflow pipette, 10 mL
Sample 0.1 mol/L NaOH