Metrohm

Application Bulletin 420/2 e

Determination of suppressor with CVS using the calibration technique «smartDT» with dynamic addition volumes

The Application Bulletin describes the determination of suppressor in acid copper baths by smartDT. The determination of suppressor with dilution titration (DT) involves numerous additions with standard solution or sample to reach the evaluation ratio. Usually fixed, equidistant addition volumes are used. With smartDT variable addition volumes are used that are dynamically calculated by the software. At the beginning the volumes are bigger. Towards the evaluation ratio the addition volume becomes smaller to guarantee a good accuracy of the result. The operator defines the first and the smallest addition volume to be used. All volumes in between are calculated by the software considering the progress of the determination.

The time saving with smartDT compared to a classic DT with fixed addition volumes can be up to 40%.

smartDT is suitable for nonlinear regression and quadratic regression as well as linear interpolation. It can be used for determination of suppressor in acid copper baths as well as in tin and tin-lead baths and works with 1, 2, and 3 mm Pt working electrodes.

An 800 Dosino is required for the automatic addition of suppressor standard or sample. The method can also be used in fully automated systems.

Content

1.1. Instruments and accessories

Quantity	Article number	
1	2.894.1210	894 Professional CVS semiautomated
1	6.5339.0X0	CVS electrode kit
1	6.6065.11X	**viva** 1.1 or higher

Fig. 1: 894 Professional CVS semiautomated

1.2. Comments

- **viva** 1.1 or higher is required for smartDT.
- For further information or details regarding operation, refer to the tutorial or manual of **viva** and the manual of the 894 Professional CVS.
- smartDT can also be carried out with a 884 Professional VA. This instrument requires the use of viva 2.0 or higher.

2. Modifying a method

The example method «AB 420 smartDT.vmet» is copied onto the hard disk of the PC when the **viva** software is installed. After importing the method into a **viva** method group it can be opened in the program part «Method». For the location of example files and the procedure to import methods into **viva,** please refer to the **viva** Help (Support ▸ How to proceed? ▸ Methods ▸ Importing a method).

«AB 420 smartDT.vmet» is an executable method to determine suppressor in acid copper bath with smartDT using Dosinos for the automatic addition of VMS and suppressor standard or sample. Commands and tracks which are related to full automation using a sample changer are not part of the method. Names of Dosing Units and solutions are defined according to the **viva** method template «Suppressor determination (CVS, DT), semiautomated» and have to be adapted where necessary.

If the method should be used directly, application specific parameters such as CVS measuring parameters, volume of VMS, concentration of the suppressor standard solution, curve type of the calibration curves, and evaluation ratio have to be adapted. For more information on these modifications please refer to the **viva** tutorial.

If a method for the determination of suppressor with classic DT is already available, this existing method can be adapted by copying individual tracks and commands from the method «AB 420 smartDT.vmet». The procedure to implement the necessary modifications into an existing method is described below.

2.1. Sample data variables

New sample data variables need to be defined in the command **START – MAIN TRACK**.

Name	*Type*	*Assignment*
Initial volume in mL	Number	ID4
Minimum volume in mL	Number	ID5

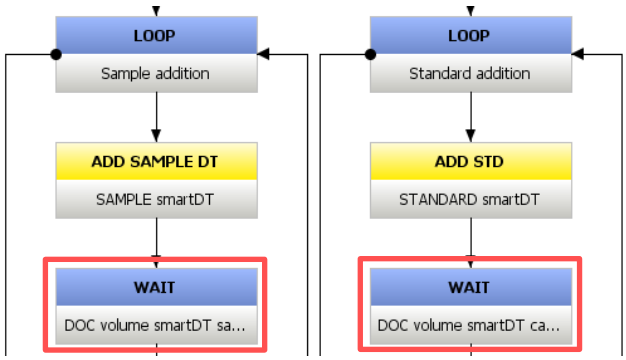
For both variables, the option «Check at start» should be active.

Note! Make sure that the spelling of the names is correct. An exact match is necessary for the calculation formulas used in the **ADD** commands.

2.2. Calibration and determination tracks

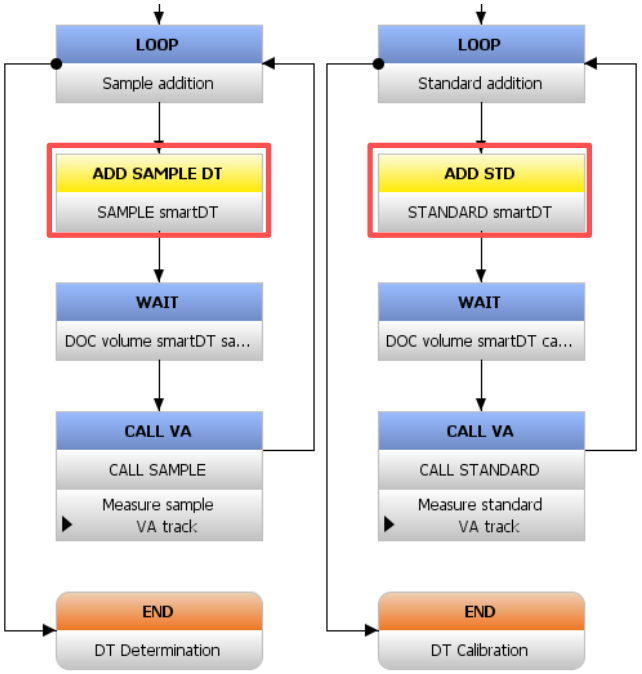
Delete the complete tracks for the calibration and for the determination in the existing method. Copy the **TRACK – DT DETERMINATION** and **TRACK – DT CALIBRATION** from the example method into the existing method. Compared to the deleted tracks, the new tracks have some additional and some modified commands.

2.2.1. Additional commands

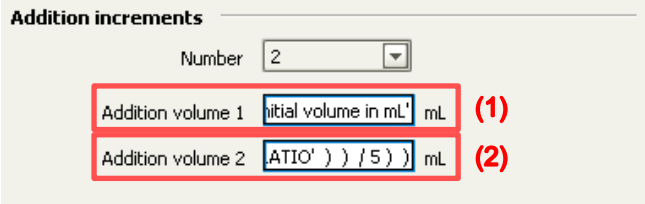


The **WAIT** commands are for documentation purposes only. The command generates a message documenting the previous addition volume. This allows to follow the development of the addition volumes during a running determination. If a live view on the addition volume is not required, the commands **WAIT – DOC VOLUME SMARTDT SAMPLE** and **WAIT – DOC VOLUME SMARTDT CALIB** may be deleted.

2.2.2. Modified commands



The commands **ADD SAMPLE DT –SAMPLE SMARTDT** and **ADD STD – STANDARD SMARTDT** have two addition increments each:



(1) Addition volume 1 is linked to the sample data variable «Initial volume in mL» thus using the volume entered on the workplace for this parameter for the first addition.

(2) Addition volume 2 incorporates a calculation formula which calculates the addition volume based on the difference between the current signal and the evaluation ratio. This formula is used for the calculation of the second and all following additions.

The basic formula for the calculation of the addition volume is:

$$\text{Addition volume x [mL]} = \text{«Minimum volume»} + \text{VEFF} * \frac{(\text{AREANORM} - \text{Evaluation ratio})}{5}$$

«Minimum volume»	Sample data variable «Minimum volume in mL»
VEFF	Projected volume at evaluation ratio
AREANORM	Standardized area of the latest signal
Evaluation ratio	Value of the evaluation ratio
5	Empiric factor

For more details on the exact formula, see «5.1. Calculation formula».

2.3. CALL commands

After inserting the new tracks, the links in the following **CALL** commands have to be reviewed.

2.3.1. START – MAIN TRACK

The command **CALL – SAMPLE OR STANDARD?** must contain the following conditions:

Track name	DT Determination
Sample type	Sample

and

Track name	DT Calibration
Sample type	Standard

2.3.2. TRACK – DT DETERMINATION and TRACK – DT CALIBRATION

The **CALL VA** commands must link to the 'Track name' of the track **VA TRACK** used in the method.

2.4. Names

2.4.1. CVS command

The name of the CVS command should be **CVS**. If a different name is used for this command, the calculation formulas in the commands **ADD SAMPLE DT – SAMPLE SMARTDT** and **ADD STD – STANDARD SMARTDT** have to be modified.

2.4.2. Substance name

The name for the substance should be «Suppressor». If a different name is used for the substance, the calculation formulas in the commands **ADD SAMPLE DT – SAMPLE SMARTDT** and **ADD STD – STANDARD SMARTDT** have to be modified.

2.4.3. Suppressor standard solution

The default name for the suppressor standard solution is «Std or sample». If a solution with a different name is used, the command **ADD STD – STANDARD SMARTDT** has to be adapted accordingly.

2.4.4. Dosing Unit for sample addition

The default name for the Dosing Unit for the addition of sample is «2 mL Standard or sample». If a Dosing Unit with a different name is used, the command **ADD SAMPLE DT – SAMPLE SMARTDT** has to be adapted accordingly.

2.5. Comments

- If the method setup is started with one of the **viva** method templates «Suppressor determination (CVS, DT), semiautomated» or «Suppressor determination (CVS, DT), automated», additional parameters may need to be modified to suit the specific application. Parameters which typically need to be adapted:
  - CVS measuring parameters
  - Volume of VMS
  - Concentration of the suppressor standard solution
  - Curve type of the calibration curves
  - Evaluation ratio
- The stop criterion in the **LOOP** commands of the example method «AB 420 smartDT.vmet» automatically adapt to the evaluation ratio. Therefore, the signal ratio Q/Q(0) is defined relative to the evaluation ratio. Parameters for «Signal assessment for DT» in the **LOOP** commands:

VA measuring command	CVS
Substance	Suppressor
Signal ratio Q/Q(0)	'ED.Calibration.CVS.Suppressor.EVRATIO' - 0.01

- The following identifiers and command names should not be changed, since it would affect the calculation formula:
  - Sample data (ID4): Initial volume in mL
  - Sample data (ID5): Minimum volume in mL
  - Substance name: Suppressor
  - **CVS – CVS**
  - **ADD STD – STANDARD SMARTDT**
  - **ADD SAMPLE DT – SAMPLE SMARTDT**

3. Example for an application

The functionality of the smartDT is shown by the model suppressor polyethylene glycol with an average molecular weight of 6000 g/mol (PEG6000).

3.1. Electrodes

WE	Driving axle Platinum electrode tip 2 mm	6.1204.510 6.1204.610
AE	Separate Pt rod electrode	6.0343.100
RE	LL Ag/AgCl reference electrode Reference electrolyte 3 mol/L KCl Electrolyte vessel Bridge electrolyte 1 mol/L KNO_3	6.0728.130 6.1245.010

3.2. Reagents

- Copper sulfate, for analysis, $CuSO_4 \cdot 5H_2O$, CAS 7758-99-8
- Sulfuric acid, for analysis, w(H_2SO_4) = 96%, CAS 7664-93-9
- Sodium chloride, for analysis, CAS 7647-14-5
- Polyethylene glycol, PEG6000, M_w(PEG6000) = 5000–7000 g/mol, for synthesis, CAS 25322-68-3
- Deionized water, type II grade (ISO 3696)

3.3. Solutions

VMS (virgin make-up solution)	β($CuSO_4 \cdot 5H_2O$) = 60 g/L σ(H_2SO_4) = 130 mL/L β(Cl^-) = 50 mg/L 60 g $CuSO_4 \cdot 5H_2O$ and 82 mg NaCl are dissolved in approx. 800 mL deionized water and filled in a 1 L volumetric flask. 130 mL H_2SO_4 are added carefully (Attention! Solution becomes very hot!). After cooling to room temperature, the solution is filled up to the mark with deionized water.

3.4. Standard solutions

Suppressor stock solution	σ(suppressor) = 1000 mL/L 2.5 g PEG6000 are dissolved and made up to 50 mL with deionized water in a volumetric flask. → β(PEG6000) = 50 g/L
Suppressor standard solution	σ(suppressor) = 5 mL/L 49.75 mL VMS is accurately dosed into a vial. 0.25 mL suppressor stock solution is pipetted into the VMS.

3.5. Check standards

Check standard 3 mL/L	σ(suppressor) = 3 mL/L 49.85 mL VMS is accurately dosed into a vial. 0.15 mL suppressor stock solution is pipetted into the VMS.
Check standard 4 mL/L	σ(suppressor) = 4 mL/L 49.8 mL VMS is accurately dosed into a vial. 0.2 mL suppressor stock solution is pipetted into the VMS.
Check standard 6 mL/L	σ(suppressor) = 6 mL/L 49.7 mL VMS is accurately dosed into a vial. 0.3 mL suppressor stock solution is pipetted into the VMS.
Check standard 7 mL/L	σ(suppressor) = 7 mL/L 49.65 mL VMS is accurately dosed into a vial. 0.35 mL suppressor stock solution is pipetted into the VMS.

3.6. Sample preparation

No sample preparation required.

3.7. Analysis

Set values for «Initial volume in mL» and «Minimum volume in mL» on the Workplace (For recommen-dations on the values for the two parameters, see «4. General Comments»).

1. Start determination.
2. 50 mL VMS are dosed into the measuring vessel.
3. Electrode is initially conditioned in VMS until the standard deviation of the signals is less than 0.5%.
4. The signal of the VMS is recorded.
5. 1st addition volume is added as defined on the Workplace for «Initial volume in mL».
6. 2nd and following addition volumes are calculated automatically by the software (for detailed information on the calculation formula see «5.1. Calculation formula»)

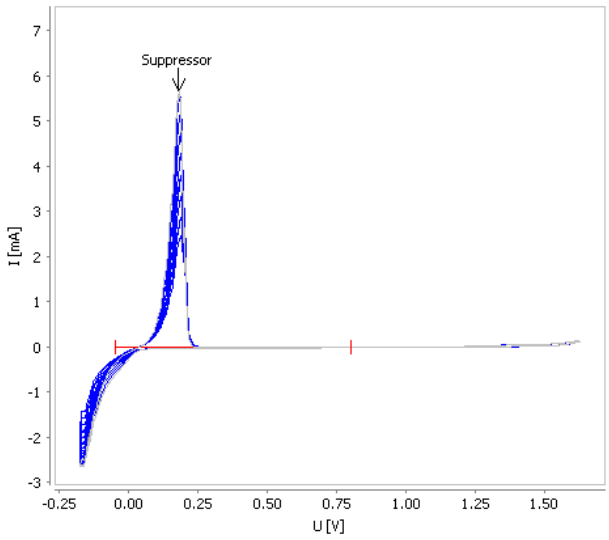
3.8. Parameters

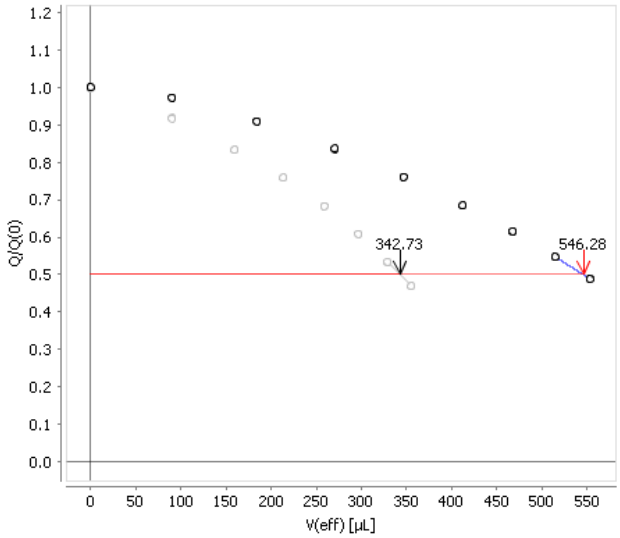
Volumes	
Volume VMS	50 mL
Addition volume (standard or sample)	Calculated (see Appendix)
Voltammetric	
Electrode	RDE
Measuring mode	CVS
Stirring speed	2500 min^{-1}
Hydrodynamic measurement	Yes
Sweep	
Start potential	1.625 V
First vertex potential	-0.175 V
Second vertex potential	1.625 V
Potential step	0.006 V
Potential step time	0.06 s
Sweep rate	0.1 V/s
No. of preparation cycles	1
No. of measuring cycles	2
Substance + calibration	
Name	Suppressor
Peak potential	0.2 V
Tolerance	0.2 V
Baseline	Horizontal Start 0.8 V End -0.05 V
Calibration method	DT (dilution titration)
Evaluation ratio	0.5
Stop criteria	0.49

3.9. Dosinos

Dosing Unit	*Cylinder volume*	*Content*
VMS	50 mL	VMS
Standard or sample	2 mL	Suppressor standard for calibration or sample for determination

3.10. Example determination





3.11. Results

Check standard	σ(suppressor)	Recovery
3 mL/L	3.14 mL/L	104.7%
4 mL/L	4.02 mL/L	100.5%
5 mL/L	5.02 mL/L	100.4%
6 mL/L	6.12 mL/L	102.0%
7 mL/L	7.18 mL/L	102.6%

4. General Comments

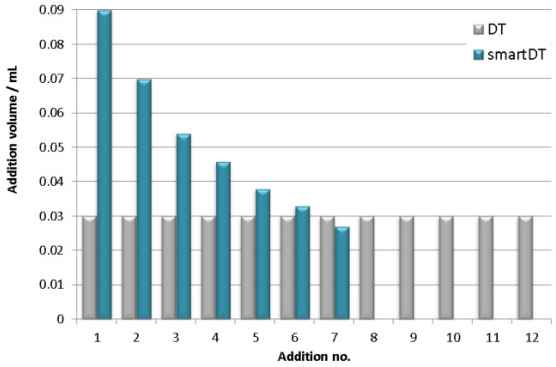
- «Initial volume in mL» defines the volume for the first addition of standard or sample. It is also used for the calculation, if the volume at the evaluation ratio cannot be predicted or does not show a reasonable value.
- Recommended value for «Initial volume in mL» is one quarter of the volume that is usually necessary to reach the evaluation ratio in the calibration. The smallest volume possible is 0.01 mL. To avoid entering too small volumes, the value for the sample data variable can be monitored, e.g.,:

Lower limit	0.01
Upper limit	1

- «Minimum volume in mL» defines the smallest volume of standard or sample to be added when the volume is calculated by the software.
- Recommended value for «Minimum volume in mL» 5 … 7% of the volume that is usually necessary to reach the evaluation ratio in the calibration. The smallest volume possible is 0.01 mL. To avoid entering too small volume the value for the sample data variable can be monitored, e.g.,:

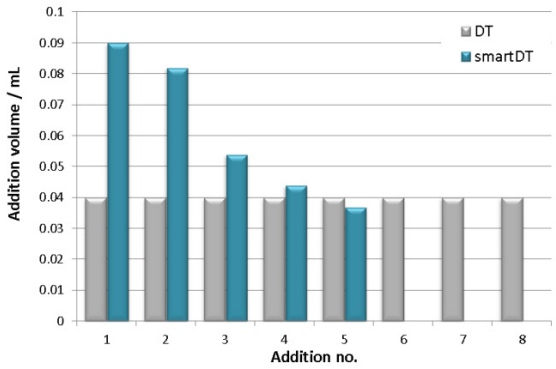
Lower limit	0.01
Upper limit	0.1

- Estimation of time saving for a calibration with σ(suppressor) = 5 mL/L (classic DT addition volume: 30 µL; smartDT: «Initial volume in mL» 0.09, «Minimum volume in mL» 0.025)



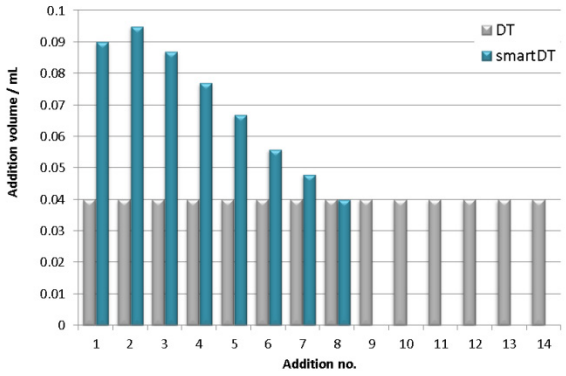
classic DT (12 additions): approx. 31 min
smartDT (7 additions): approx. 21 min
time saving: 32%

- Estimation of time saving for a determination of a sample with σ(suppressor) = 6 mL/L (classic DT addition volume: 40 µL; smartDT: «Initial volume in mL» 0.09, «Minimum volume in mL» 0.035)



classic DT (8 additions): approx. 23 min
smartDT (5 additions): approx. 17 min
time saving: 26%

- Estimation of time saving for a determination of a sample with σ(suppressor) = 3 mL/L (classic DT addition volume: 40 µL; smartDT: «Initial volume in mL» 0.09, «Minimum volume in mL» 0.035)



classic DT (14 additions):	approx. 35 min
smartDT (8 additions):	approx. 23 min
time saving:	34%

- If the smartDT is done in a sample series with a fully automated system, the display of ID4 and ID5 in the sample table has to be activated first. To display the two additional IDs, go to the **viva** «Workplace» and select the «Determination series» tab in the «Run» window. Under «Sample table ▸ Properties» the display of ID4 and ID5 is activated with check boxes.

5. Appendix

5.1. Calculation formula

Basic formula for the calculation of the addition volume:

$$\text{Addition volume x [mL]} = \text{«Minimum volume»} + \text{VEFF} * \frac{(\text{AREANORM} - \text{Evaluation ratio})}{5}$$

Formula used in the command **ADD SAMPLE DT – SAMPLE smartDT**

```
'SD.Minimum volume in mL'  + ( Case( Abs( 'RS.CVS.Suppressor.VEFFSMPL' * 1000 ) <= 'SD.Initial volume in
mL' * 7 ; Abs( 'RS.CVS.Suppressor.VEFFSMPL' * 1000 ) ; 'SD.Initial volume in mL' * 7 ; 'SD.Initial volume
in mL' * 7 ) * ( ( Abs( 'RS.CVS.Suppressor.VAR{ Round('SAMPLE smartDT.ACO' - 1 ) }.REP{1}.AREANORM' -
'ED.Calibration.CVS.Suppressor.EVRATIO' ) ) / 5 ) )
```

Formula used in the command **ADD STD – STANDARD smartDT**

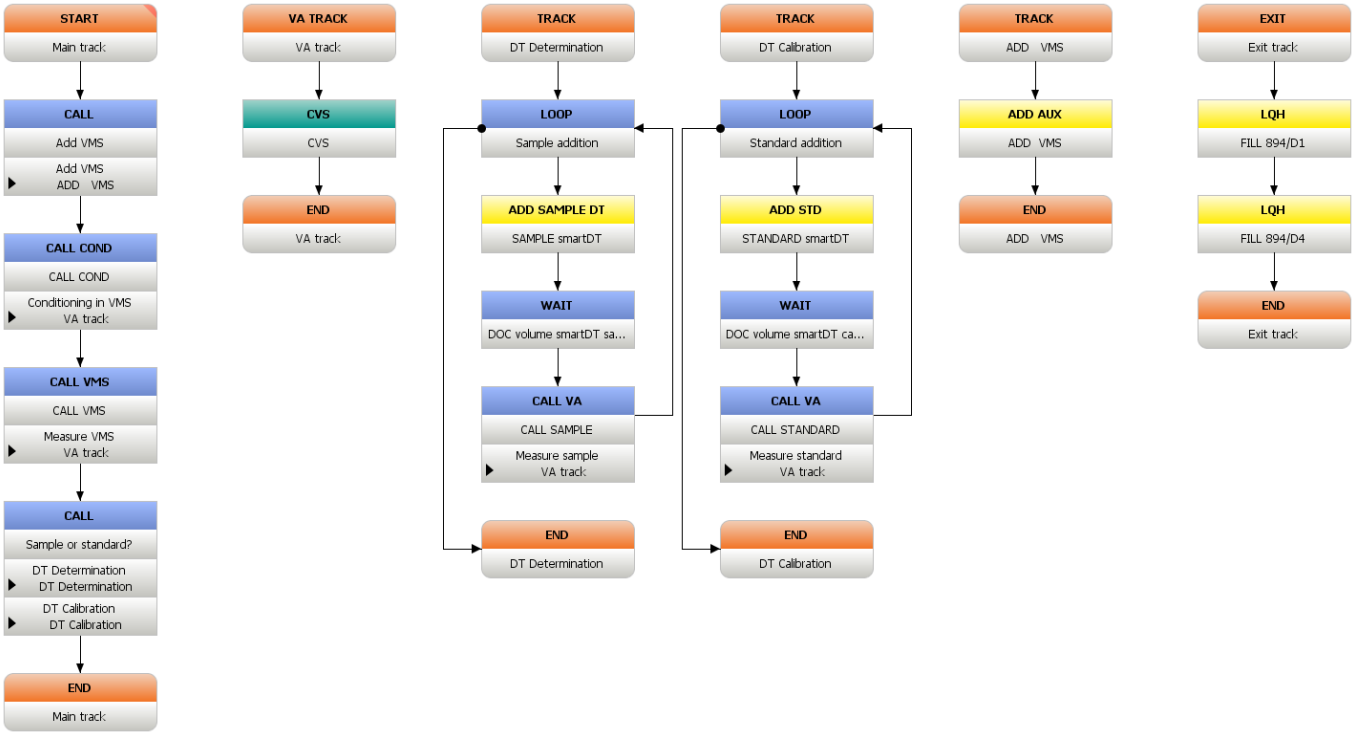
```
'SD.Minimum volume in mL' + ( Case( Abs( 'RS.CVS.Suppressor.VEFFSTD' * 1000 ) <= 'SD.Initial volume in mL'
* 7 ; Abs( 'RS.CVS.Suppressor.VEFFSTD' * 1000 ) ; 'SD.Initial volume in mL' * 7 ; 'SD.Initial volume in
mL' * 7 ) * ( ( Abs( 'RS.CVS.Suppressor.VAR{ Round('STANDARD smartDT.ACO' - 1 ) }.REP{1}.AREANORM' -
'ED.Calibration.CVS.Suppressor.EVRATIO' ) ) / 5 ) )
```

Transfer of the basic formula to **viva**:

Basic formula	***viva***
Addition volume x [mL] x - addition number	Calculated addition volume has to be in milliliter (mL)
«Minimum volume»	'SD.Minimum volume in mL' Volume in milliliter (mL) as defined on the Workplace
VEFF projected volume at evaluation ratio	Case(Abs('RS.CVS.Suppressor.VEFFSTD' * 1000) <= 'SD.Initial volume in mL' * 7 ; Abs('RS.CVS.Suppressor.VEFFSTD' * 1000) ; 'SD.Initial volume in mL' * 7 ; 'SD.Initial volume in mL' * 7 ('RS.CVS.Suppressor.VEFFSTD' * 1000) or ('RS.CVS.Suppressor.VEFFSMPL' * 1000) – Result variable which reads out the projected volume at evaluation ratio in mL for the standard (VEFFSTD) or the sample (VEFFSMPL). Multiplication with 1000 is required since the base unit for the variable is liter (L). Abs(…) – Function which handles the case that the projected volume gets negative. → Always the absolute value of VEFF is used for the calculation. Case(…) – Function which handles the case that VEFF cannot be calculated or gets disproportionally high. → In these cases ('SD.Initial volume in mL' * 7) is used for calculation, 7 is an empirical value. 'SD.Initial volume in mL' – Sample data variable which reads out the volume in mL as defined on the Workplace
AREANORM Standardized area of the latest peak	Abs('RS.CVS.Suppressor.VAR{ Round('STANDARD smartDT.ACO' - 1) }.REP{1}.AREANORM' - 'ED.Calibration.CVS.Suppressor.EVRATIO') 'RS.CVS.Suppressor.VAR{x}.REP{y}.AREANORM' – Result variable which reads out the standardized signal area of a specific curve, specified by variation (VAR{x}) and replication (REP{y}). Var{x} – Variation x of the CVS curves from which the area should be used for calculation, x reflects the addition number. *.ACO – addition counter Round(…) – Function which is necessary to avoid decimal places in the calculation of the variation.

	REP{1} – Replication 1 of the CVS curves of the respective addition; since there is mostly only a small difference between first and second replication only the first replication is considered to keep the formula simple Abs(…) – Function which handles the case AREANORM < evaluation ratio.
Evaluation ratio	'ED.Calibration.CVS.Suppressor.EVRATIO' Evaluation parameter variable for «Evaluation ratio» used in the application
5	5 Empirical factor which has an influence on the number of additions. This parameter can be adapted, if necessary. A smaller value results in fewer additions, a bigger value in more additions. Useful values are 3 … 6.

5.2. Method sequence



5.3. Example determination

viva

Result report
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2015-04-14 15:27:26
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Determination

Determinaton start	2015-04-14 14:22:32 UTC+2
User name (short)	Metrohm
User name	Metrohm International Headquarters
Method name	AB 420 smartDT

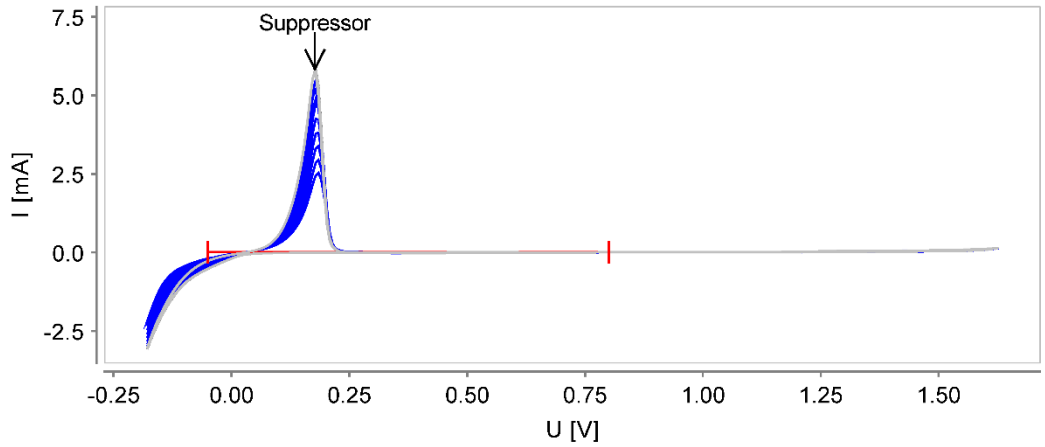
Sample data

Sample type	Sample
ID 1	Determination smartDT
ID 2	Standard 3 mL/L
ID 3	Suppressor PEG
Initial volume in mL	0.09
Minimum volume in mL	0.035

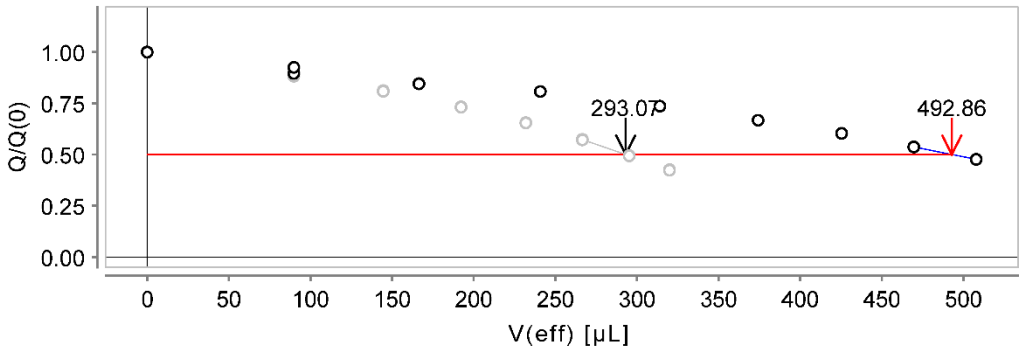
Results overview

CVS.Suppressor.Concentration	2.97	mL/L
CVS.Suppressor.Concentration.ASD	4.76	µL/L
CVS.Suppressor.Concentration.RSD	0.2	%

CVS



CVS (Suppressor)



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Concentration	*2.97 mL/L*
Absolute standard deviation	*0.00 mL/L*
Relative standard deviation	*0.2 %*
Function	*y = 1.281E0 - 1.584E3 * x*
Evaluation quantity	*Area*
Curve type	*Linear interpolation*
Weighting	*used*
Calibration factor	*29.14 µL/L*
Date calibration	*2015-04-14 09:58:55 UTC+2*
Determination ID calibration	*3dada3a8:14cb1904d3e:-78a0*

CALL	Var	Rep	Peak potential [V]	Area [mC]	Used
CALL VMS		1	0.177	3.15	used
CALL VMS		2	0.177	3.15	used
CALL SAMPLE	1	1	0.178	2.92	used
CALL SAMPLE	1	2	0.177	2.82	used
CALL SAMPLE	2	1	0.178	2.66	used
CALL SAMPLE	2	2	0.178	2.67	used
CALL SAMPLE	3	1	0.179	2.55	used
CALL SAMPLE	3	2	0.179	2.54	used
CALL SAMPLE	4	1	0.180	2.32	used
CALL SAMPLE	4	2	0.180	2.32	used
CALL SAMPLE	5	1	0.181	2.10	used
CALL SAMPLE	5	2	0.181	2.10	used
CALL SAMPLE	6	1	0.182	1.90	used
CALL SAMPLE	6	2	0.182	1.90	used
CALL SAMPLE	7	1	0.182	1.69	used
CALL SAMPLE	7	2	0.182	1.69	used
CALL SAMPLE	8	1	0.182	1.50	used
CALL SAMPLE	8	2	0.182	1.50	used

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Messages

Main track - CALL COND

Message date . . . . . 2015-04-14 14:29:28 UTC+2
Message title . . . . . Command canceled
Message text . . . . . Command 'CALL COND': The 'Evaluation quantity' stop criterion defined in the command has been met. The command has been canceled.

DT Determination - DOC volume smartDT sample

Message date . . . . . 2015-04-14 14:31:37 UTC+2
Message title . . . . .
Message text . . . . . Addition volume 1: 0.09 mL

DT Determination - DOC volume smartDT sample

Message date . . . . . 2015-04-14 14:33:44 UTC+2
Message title . . . . .
Message text . . . . . Addition volume 2: 0.077 mL

DT Determination - DOC volume smartDT sample

Message date . . . . . 2015-04-14 14:35:52 UTC+2
Message title . . . . .
Message text . . . . . Addition volume 3: 0.075 mL

DT Determination - DOC volume smartDT sample

Message date . . . . . 2015-04-14 14:37:59 UTC+2
Message title . . . . .
Message text . . . . . Addition volume 4: 0.074 mL

DT Determination - DOC volume smartDT sample

Message date . . . . . 2015-04-14 14:40:06 UTC+2
Message title . . . . .
Message text . . . . . Addition volume 5: 0.061 mL

DT Determination - DOC volume smartDT sample

Message date . . . . . 2015-04-14 14:42:13 UTC+2
Message title . . . . .
Message text . . . . . Addition volume 6: 0.052 mL

DT Determination - DOC volume smartDT sample

Message date . . . . . 2015-04-14 14:44:20 UTC+2
Message title . . . . .
Message text . . . . . Addition volume 7: 0.045 mL

DT Determination - DOC volume smartDT sample

Message date . . . . . 2015-04-14 14:46:26 UTC+2
Message title . . . . .
Message text . . . . . Addition volume 8: 0.039 mL

DT Determination - Sample addition

Message date . . . . . 2015-04-14 14:48:30 UTC+2
Message title . . . . . Command canceled
Message text . . . . . Command 'Sample addition': The defined stop criterion 'Signal assessment for DT' has been met with the value '0.48'. The command has been canceled.

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