

Correction strategies in deuterium analysis using chromium reduction

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Introduction

High precision deuterium isotope analysis (D/H) of water is routinely carried out by using a hot chromium reactor. For these measurements, three post run corrections have to be applied to the raw data:

- (1) Memory correction
- (2) Drift correction
- (3) Normalization to the VSMOW/SLAP scale

One crucial point is to observe and correct for the machine drift (Fig. 1). Consequently, different strategies for drift correction were proposed (e.g. Nelson and Dettman, 2001; Werner and Brand, 2001; Brooks et al., 2004). In this study, different correction approaches were tested for their influence on quality control and their usability in day to day analysis.

Results

Reactor Types

Reactors with different packing were reheated several times. It turned out that reheating of reactors has no influence on the reproducibility of the lab standards, as long as proper vacuum is maintained during cooling and some “dummy” injections are made after reheating. Fig. 2 shows typical examples of the observed drift for both reactor types in the used DI-IRMS system.

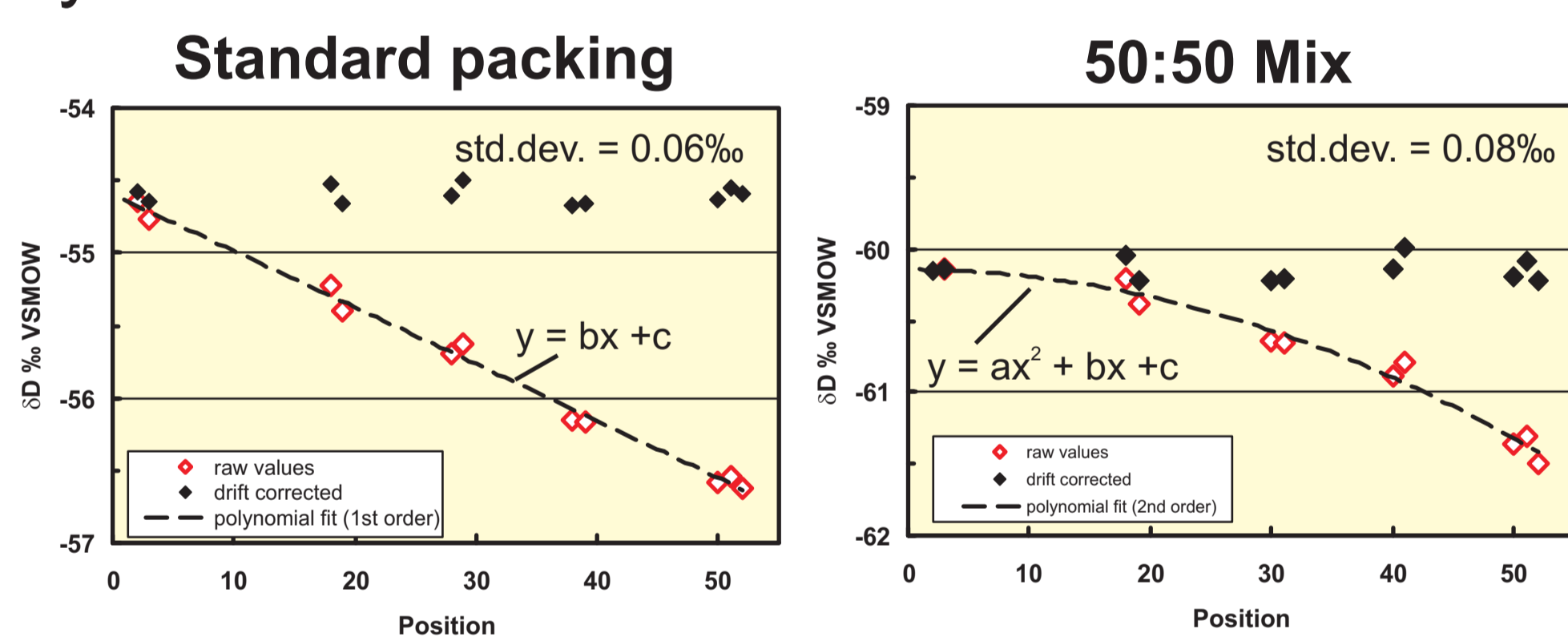


Fig. 2: Typical drift observed with different reactor packings. Standard deviation after drift correction is typically < 0.2‰.

Discussion

As long as the raw values of the drift control standard show continuously lower values during the sequence, the Rayleigh and polynomial corrections yield comparable results. In case of no or only minor drift in the first part of the sequence, the Rayleigh correction can not fit the data properly due to mathematical reasons. Therefore, a polynomial correction function was chosen for the standardized spread sheet shown in Fig. 4.

	Y	Z	IA	AB	AC	AD	AE	AF	AG	AH
1	ErrorProcedure108	raw δD	memory	memory	memory	memory	memory	memory	memory	memory
2	0.21	dest H2O	-59.46	fixrat.	-59.46	fixrat.	-59.52	fixrat.	-59.52	fixrat.
3	0.19	dest H2O	-59.19	1.350	-59.19	-0.00293	-59.29	-59.29	1.0185	-56.36
4	0.15	ANTA -I	-256.79	second	-256.81	-0.00293	-256.45	-256.45	second	-257.17
5	0.14	ANTA -I	-256.83	0.005	-256.87	0.00574	-256.06	-256.06	4.0252	-257.79
6	0.13	ANTA -I	-256.77	second	-256.77	0.00574	-256.99	-256.99	second	-257.72
7	0.16	ANTA -I	-257.38	second	-257.38	0.00574	-257.63	-257.63	second	-258.97
8	0.10	SLAP	-421.96	second	-424.10	0.14	-424.37	-424.37	second	-428.20
9	0.13	SLAP	-424.14	second	-424.17	0.14	-424.47	-424.47	second	-428.30
10	0.14	SLAP	-423.44	second	-423.43	0.14	-423.75	-423.75	second	-427.56
11	0.14	HIS-III	-16.46	second	-11.17	0.14	-11.50	-11.50	second	-7.68
12	0.18	HIS-III	-11.77	second	-11.71	0.14	-12.05	-12.05	second	-8.24
13	0.13	HIS-III	-11.68	second	-11.68	0.14	-12.01	-12.01	second	-8.21
14	0.12	HIS-III	-11.53	second	-11.53	0.14	-11.86	-11.86	second	-8.05
15	0.10	HIS-III	-11.12	second	-11.11	0.14	-11.44	-11.44	second	-7.62
16	0.10	SKOW	-3.79	second	-3.70	0.14	-4.01	-4.01	second	-0.06
17	0.20	SKOW	-3.64	second	-3.64	0.14	-3.94	-3.94	second	0.02
18	0.16	SKOW	-3.64	second	-3.64	0.14	-3.91	-3.91	second	0.04
19	0.16	dest H2O	-59.20	second	-59.99	0.14	-59.24	-59.24	second	-56.31
20	0.14	dest H2O	-59.14	second	-59.15	0.14	-59.37	-59.37	second	-56.44

Fig. 4: Standardized Excel spread sheet for deuterium post run corrections. The data sheet can be imported directly in the “LabData” data base system (Suckow and Dumke, 2001) for data storage and further evaluation.

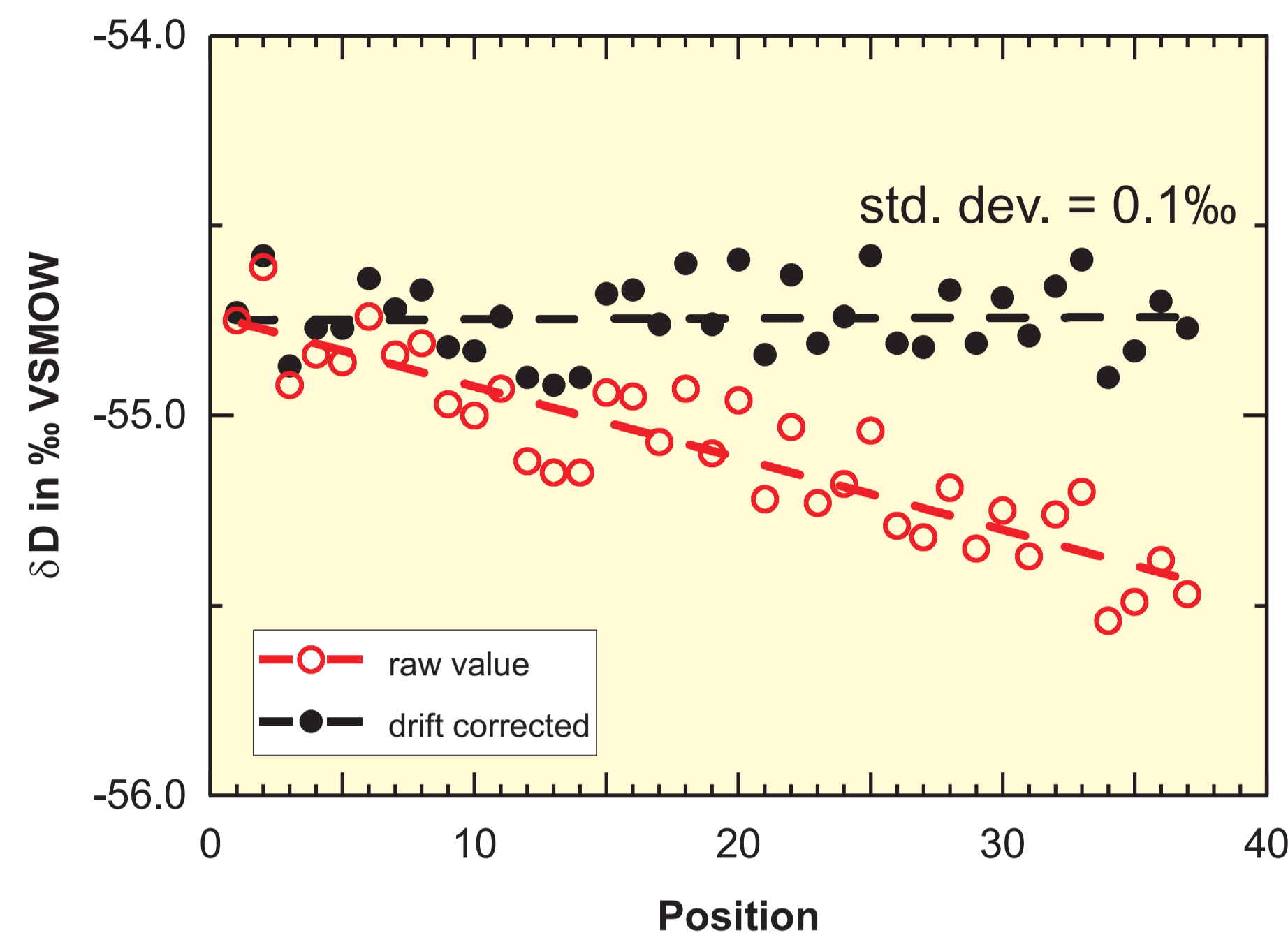


Fig. 1: Drift observed during a sequence of 37 injections (~10 h) of a drift control standard (raw values). A reactor with standard packing (<100mesh) was used. The drift follows a simple linear function.

Correction functions

According to theory, the drift should mainly be caused by the fractionation of the standard gas in the reference bellow. Therefore, the drift should follow a Rayleigh fractionation process according to

$$\delta D = (\delta D_0 + 1000) f^{(\alpha-1)} - 1000 \quad (1)$$

where f is the fraction remaining, α the fractionation factor, δD_0 the initial composition of the reference gas and δD the composition for a given f value.

Visual evaluation of the runs implies that the drift follows a polynomial function (1st or 2nd order, Fig. 2, Fig. 3)

$$ax^2 + bx + c \quad (2)$$

with the coefficients a , b and c .

A comparison of the two functions for different run characteristics is shown in Fig. 3.

Reproducibility

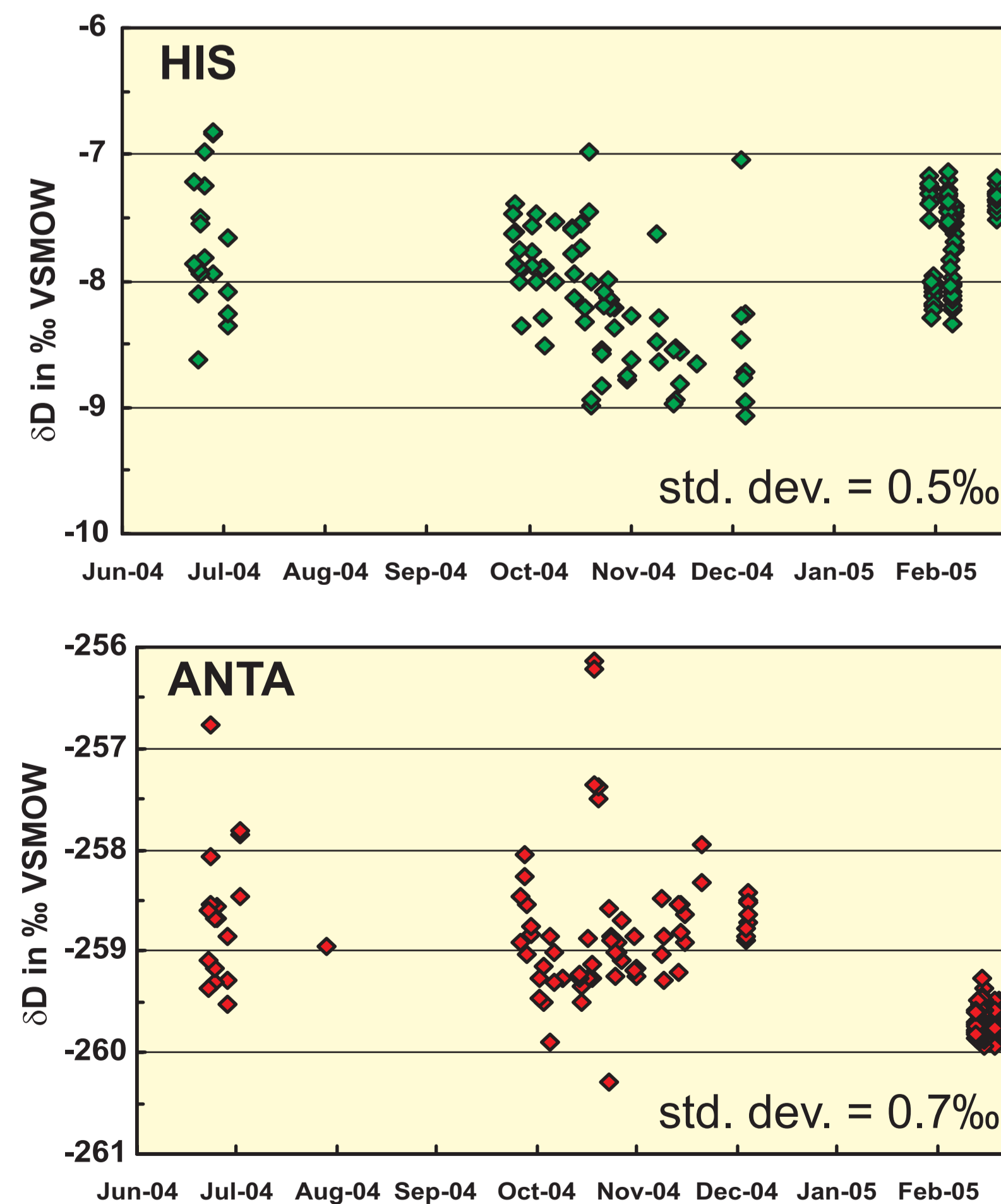


Fig. 5: External reproducibility of two quality control standards with different isotopic compositions. Both were treated as unknowns. The drift control standard (δD = -56.5‰ VSMOW) had a standard deviation of 0.3‰ for the shown time interval.

Methods

Water samples were analyzed for δD using a fully automated chromium reduction system at 800°C (H/Device, ThermoFinnigan) directly coupled to the dual inlet (DI) system of a Finnigan Delta S isotope ratio mass spectrometer (IRMS). Typical run time for one sequence with 52 samples was 12h-14h.

Reactor types

Two different types of reactor packings were used: The “standard” packing with <100mesh chromium metal powder (from Alfa Aesar) and the 50:50 mixture of <325mesh and <100mesh chromium powder, as proposed by Nelson and Dettman (2001) which allows more than 1500 injections.

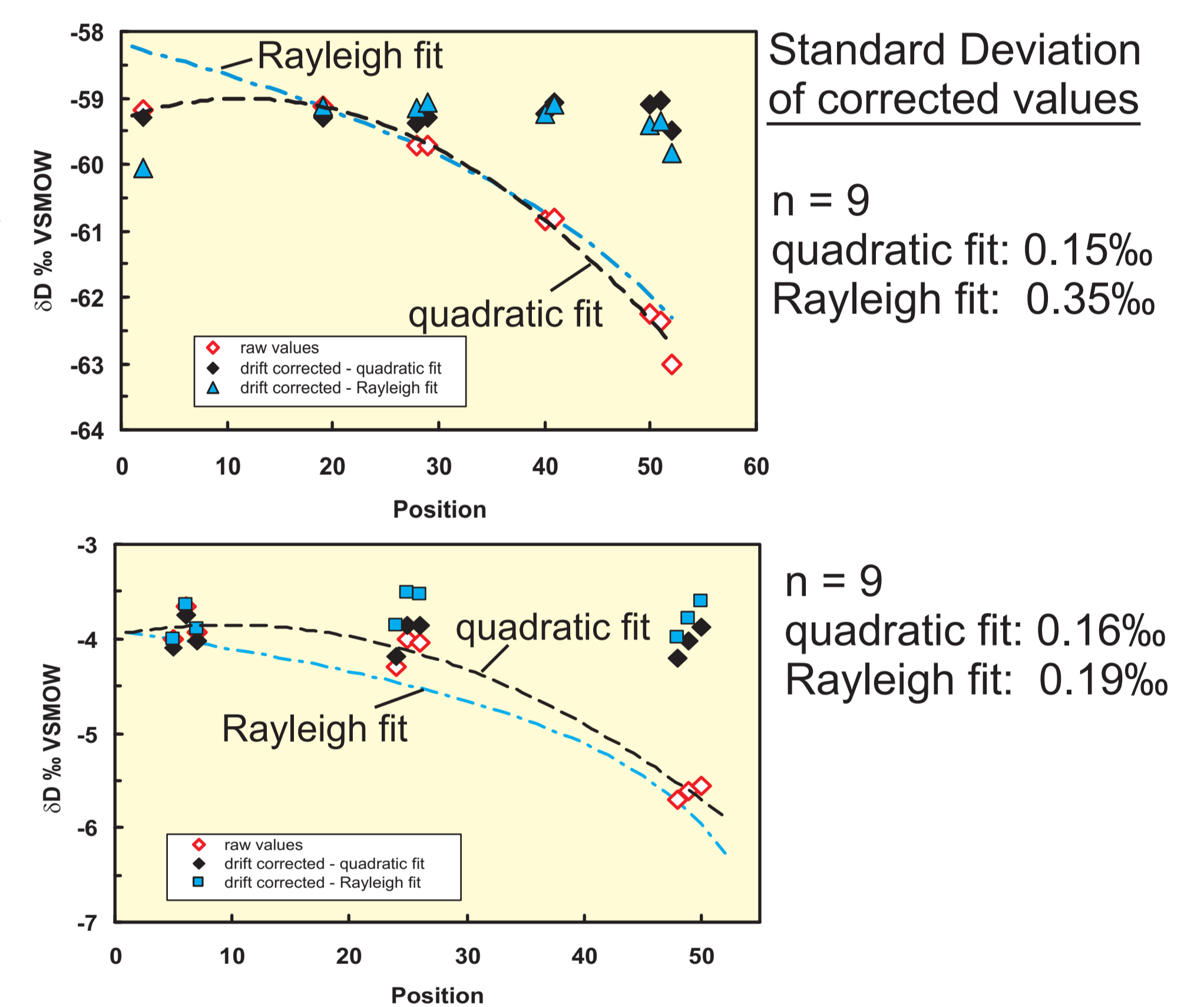


Fig. 3: A correction based on a Rayleigh fractionation yields poor results in case of a (near) horizontal shape of the drift control in the first part of the sequence.

Conclusions

- ✗ The drift in each sequence has to be corrected by a regression fitted to a drift control standard.
- ✗ Evaluation of several runs and different correction functions showed that a second order polynomial regression yields the best results.
- ✗ The results show that an external precision, defined as standard deviation of the control standards during all runs, of 0.5‰ can be achieved in routine analysis if this standardized polynomial drift correction is applied.

References

- Brooks, P.D., He, S. Dillion, P. and Dawson, T.E. (2004), *JESIUM Conference 2004*, Vienna.
 Nelson, S.T. and Dettman D. (2001), *Rapid. Comm. Mass Spec.* **15**, 2301-2306
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