

Dithiocarbamates

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Previous proficiency tests: lessons learned

- Rapid breakdown of dithiocarbamates in aqueous solutions [1].
- The degradation product CS₂ is highly volatile.
- Reaction kinetics are highly influenced by temperature.
- ➔ Significant losses of dithiocarbamates are reported during test material preparation by different PT providers [2–7].



Preparation at room temperature:

- ➔ Loss of up to 100 % during homogenisation [2].



PT providers usually prepare test materials of dithiocarbamates while cooling with dry ice (-78°C).

- ➔ Degradation of > 40 % [3], 70 % [4, 5] or even up to 80 % [9] of the spiked dithiocarbamates.
- ➔ Dry ice is not cold enough to completely avoid degradation.

Technical improvements

Temperature

From 2015 on, liquid nitrogen (-195 °C) is used throughout the whole process of test material preparation in PROOF-ACS PTs related to dithiocarbamates [7–9].



- ➔ Homogenisation, spiking and sub-sampling is feasible without degradation / loss of CS₂.
- ➔ Recoveries of the spiked levels are close to 100 % in strawberries, tomatoes and raspberries [8, 9].



Influence of pH

DT50 values of thiram in aqueous solutions (all @ 25 °C) [1, 10]:

- 68.5 days @ pH 5
- 3.5 days @ pH 7
- 6.9 hours @ pH 9



- ➔ High impact of different pH values of fruits and vegetables on degradation of dithiocarbamates.

Lessons learned from P1510-RT and P1624-RT [7, 8]:

Liquid nitrogen is used during preparation of both homogenates.

- ➔ Matrix strawberry: 95 % recovery of the spiked level.
- ➔ Matrix lettuce: 11 % recovery of the spiked level.

pH (lettuce): 5.8–6.1 >> pH (strawberry): 3.0–3.9 [11, 12].

- ➔ High impact of pH on the stability of thiram.
- ➔ Adjust pH if necessary.

Texture

- Usually frozen homogenates are provided in PTs.
- Handling differs from the routine procedures.
- Freeze-thaw cycles in the labs are a major source of error in PTs.
- ➔ A fine, powdery material, which can be taken of the box without freeze-thawing cycles is provided in P1715-RT (see picture below).



How to improve dithiocarbamates PTs

Due to the low recoveries, the comparability criterion (z-score) is applied for evaluation in common PTs. Thus,

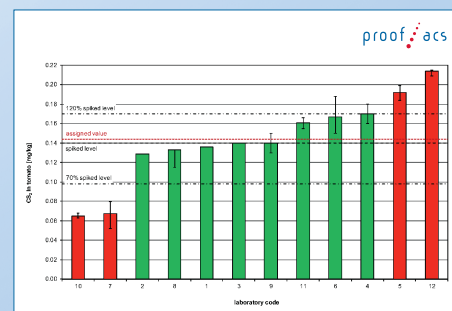
- the outcome of the PT highly depends on the quality of the submitted results.
- laboratories, which found a proper way to avoid degradation might be punished with z-scores > 2 even though their results are closer to the true dithiocarbamate content in the sample.
- ➔ Analytical results should not only be comparable, but reflect the true dithiocarbamate content in the sample.

To do:

1. Preparation of a spiked test material without degradation of dithiocarbamates.
2. Application of the trueness criterion for evaluation.

Proof of concept – P1715-RT

- No degradation of thiram in both test materials (raspberry/tomato) [9].
- The trueness criterion is applied for evaluation: results within 70 to 120 % of the spiked level are considered satisfying.
- Test material tomato: eight out of twelve laboratories reported satisfying results. The assigned value is 103 % of the spiked level of 0.14 mg/kg.
- Results are similar related to the test material raspberry (not shown, assigned value: 106 % of the spiked level of 0.088 mg/kg).



P1715-RT: Test material tomato [9].

Summary

- Homogenisation and spiking of test samples is feasible without losing CS₂.
- Use liquid nitrogen to control temperature.
- Adjust pH.
- Powdery material should be preferred to avoid freeze-thaw-cycles.
- Dithiocarbamate PTs are an artificial situation. The sample preparation, with a high impact on the quality of the analytical results is not part of the PT. Instead, a powdery test sample is provided. The robust standard deviations and the recoveries of the spiked levels thus reflect the analytical part of the dithiocarbamate analysis only.
- The findings on the behaviour of dithiocarbamates during the preparation of PT samples should build the basis for a discussion of the sample preparation of dithiocarbamates in routine. It should be questioned if and how the sample preparation procedure of dithiocarbamates can be improved in routine analysis.

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