

**Quantitative Determination of Spermidine in 50 German Cheese Samples on a Core-Shell Column by High-Performance Liquid Chromatography with a Photodiode Array Detector Using a Fully Validated Method**

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**Table S1.** Intra- and Interday Recovery, Precision and Accuracy Values for **8** on Three Consecutive Days with Low, Medium, and High Concentrations (0.08, 0.8, 4 mg/L; n = 5) Added to Deichgraf Cheese Samples.

|          | Concentration<br>(mg/L) | Recovery<br>(%) | Precision<br>(% CV) | Accuracy<br>(bias %) |
|----------|-------------------------|-----------------|---------------------|----------------------|
| intraday | 0.08                    | 102.6 ± 6.49    | 6.82                | 1.79                 |
|          | 0.80                    | 91.4 ± 3.51     | 3.79                | -8.67                |
|          | 4.00                    | 100.6 ± 3.35    | 3.23                | 0.63                 |
| interday | 0.08                    | 99.2 ± 8.05     | 5.53                | -1.00                |
|          | 0.80                    | 87.7 ± 3.20     | 2.78                | -12.30               |
|          | 4.00                    | 95.6 ± 5.99     | 2.83                | -3.46                |

CV: coefficient of variation

**Table S2.** Standard Solution Stabilities of **8** Standards at Low, Medium, and High Concentrations (0.08, 0.8, 4 mg/L) after Short- (24 h) and Long-term (1 month) Storage at Different Temperatures (n = 5).

|                                     | Concentration<br>(mg/L) | Increase/decrease<br>(%) | Precision<br>(% CV) |
|-------------------------------------|-------------------------|--------------------------|---------------------|
| <b>Short-term stability: RT</b>     | 0.08                    | 2.20                     | 3.82                |
|                                     | 0.8                     | -5.43                    | 14.2                |
|                                     | 4                       | -5.59                    | 6.80                |
| <b>Short-term stability: 4 °C</b>   | 0.08                    | -1.64                    | 1.24                |
|                                     | 0.8                     | 0.69                     | 5.57                |
|                                     | 4                       | 1.49                     | 4.00                |
| <b>Short-term stability: -20 °C</b> | 0.08                    | -2.34                    | 12.9                |
|                                     | 0.8                     | -0.61                    | 9.88                |
|                                     | 4                       | 0.61                     | 9.01                |
| <b>Short-term stability: -80 °C</b> | 0.08                    | -2.79                    | 12.8                |
|                                     | 0.8                     | -2.53                    | 3.71                |
|                                     | 4                       | 0.36                     | 4.22                |
| <b>Long-term stability: -20 °C</b>  | 0.08                    | 3.82                     | 3.54                |
|                                     | 0.8                     | 2.23                     | 2.17                |
|                                     | 4                       | -3.36                    | 5.49                |
| <b>Long-term stability: -80 °C</b>  | 0.08                    | 5.33                     | 3.29                |
|                                     | 0.8                     | 3.93                     | 7.44                |
|                                     | 4                       | -4.73                    | 7.50                |

CV: coefficient of variation, RT: room temperature

**Table S3.** Short- (24 h) and Long-term (1, 2, 3 months) Stabilities at Different Storage Temperatures, Freeze-Thaw and Benchtop Stabilities of **8** Spiked Cheese (Deichgraf; 0.08, 0.8, 4 mg/L) Samples (n = 4-5).

|                                       | Concentration<br>(mg/L) | Increase/decrease<br>(%) | Precision<br>(% CV) |
|---------------------------------------|-------------------------|--------------------------|---------------------|
| <b>Short-term stability (24 h)</b>    |                         |                          |                     |
| RT                                    | 0.08                    | -11.9                    | 6.02                |
|                                       | 0.8                     | -5.68                    | 14.3                |
|                                       | 4                       | -7.56                    | 2.30                |
| 4 °C                                  | 0.08                    | -16.1                    | 2.62                |
|                                       | 0.8                     | -9.18                    | 8.49                |
|                                       | 4                       | -1.09                    | 12.4                |
| -20 °C                                | 0.08                    | -2.32                    | 16.7                |
|                                       | 0.8                     | -10.2                    | 14.1                |
|                                       | 4                       | -3.25                    | 14.7                |
| -80 °C                                | 0.08                    | -10.6                    | 0.72                |
|                                       | 0.8                     | -4.46                    | 3.27                |
|                                       | 4                       | -4.49                    | 13.1                |
| <b>Long-term stability (1 month)</b>  |                         |                          |                     |
| -20 °C                                | 0.08                    | -11.3                    | 4.20                |
|                                       | 0.8                     | -0.20                    | 1.84                |
|                                       | 4                       | -6.89                    | 5.99                |
| -80 °C                                | 0.08                    | -22.1                    | 1.66                |
|                                       | 0.8                     | -3.81                    | 4.82                |
|                                       | 4                       | -8.84                    | 7.04                |
| <b>Long-term stability (2 months)</b> |                         |                          |                     |
| -20 °C                                | 0.08                    | -8.69                    | 12.7                |
|                                       | 0.8                     | -4.79                    | 5.15                |
|                                       | 4                       | 1.74                     | 12.7                |
| -80 °C                                | 0.08                    | -2.19                    | 18.3                |
|                                       | 0.8                     | -9.76                    | 10.1                |
|                                       | 4                       | 6.91                     | 7.83                |
| <b>Long-term stability (3 months)</b> |                         |                          |                     |
| -20 °C                                | 0.08                    | -4.01                    | 2.51                |
|                                       | 0.8                     | -1.17                    | 6.49                |
|                                       | 4                       | -14.8                    | 8.06                |
| -80 °C                                | 0.08                    | -8.28                    | 3.02                |
|                                       | 0.8                     | -1.12                    | 5.58                |
|                                       | 4                       | -5.76                    | 14.1                |
| <b>Three F/T cycles</b>               | 0.08                    | -7.86                    | 6.22                |
|                                       | 0.8                     | -12.4                    | 11.0                |
|                                       | 4                       | -7.57                    | 7.86                |
| <b>Benchtop Stability at RT</b>       |                         |                          |                     |
| 6 h                                   | 0.08                    | -5.92                    | 7.92                |
|                                       | 4                       | -3.85                    | 9.26                |
| 12 h                                  | 0.08                    | -8.40                    | 7.97                |
|                                       | 4                       | -6.50                    | 11.4                |
| 18 h                                  | 0.08                    | -11.8                    | 9.86                |
|                                       | 4                       | -7.08                    | 13.3                |
| 24 h                                  | 0.08                    | -17.5                    | 4.64                |
|                                       | 4                       | -9.10                    | 8.09                |

CV: coefficient of variation, RT: room temperature, F/T: freeze and thaw