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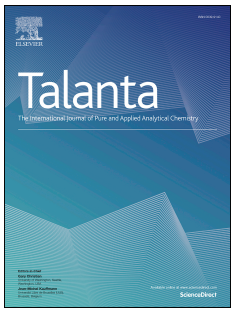

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Evaluation of a calibration transfer between a benchtop and portable Mid-InfraRed spectrometer for cocaine classification and quantification

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Abstract

A portable Fourier Transform mid-InfraRed (FT-MIR) spectrometer using Attenuated Total Reflectance (ATR) sampling is used for daily routine screening of seized powders. Earlier, ATR-FT-MIR combined with Support Vector Machines (SVM) algorithms resulted in a significant improvement of the screening method to a reliable and straightforward classification and quantification tool for both cocaine and levamisole. However, can this tool be transferred to new (hand-held) devices, without loss of the extensive dataset? The objective of this study was to perform a calibration transfer between a newly purchased bench-top (BT) spectrometer and a portable (P) spectrometer with existing calibration models. Both instruments are from the same brand and have identical characteristics and acquisition parameters (FT instrument, resolution of 4 cm^{-1} and wavenumber range 4000 to 500 cm^{-1}). The original SVM classification model (n=515) and SVM quantification model (n=378) were considered for the transfer trial.

Three calibration transfer strategies were assessed: 1) adjustment of slope and bias; 2) correction of spectra from the new instrument BT to P using piecewise direct standardization (PDS) and 3) building a new mixed instrument model with spectra of both instruments. For each approach, additional cocaine powders were measured (n=682) and the results were compared with GC-MS and GC-FID.

The development of a mixed instrument model was the most successful in terms of performance. The future strategy of a mixed model allows applying the models, developed in the laboratory, to portable instruments that are used on-site, and vice versa.

The approach offers opportunities to exchange data within a network of forensic laboratories using other FT-MIR spectrometers.

Keywords: calibration transfer, portable, FT-MIR, SVM, powder, cocaine

instrument P

instrument BT

calibration models:

- cocaine detected/not detected
- estimation purity

new samples

predict new samples instrument BT with mixed model instrument P+BT

Introduction

Mid-infrared spectroscopy (MIR) has become an important technique for the identification of narcotic and psychoactive substances by border control authorities, law enforcement and forensic institutes. Since borders are important gateways for the entrance of illicit drugs and their precursors, border control authorities are facing major challenges to obtain accurate and fast results on-site. Currently used on-site detection methods are usually fast but lack specificity, which makes laboratory confirmation analyses still imperative.

The combination of MIR with chemometrics has shown to be a useful and reliable tool for both the identification and quantification of cocaine and levamisole in powders [1, 2]. An important limitation is the fact that these developed chemometric models are related to the instrument where the spectra are recorded on. Consequently, these models are not transferable as such to a new device. The models become invalid due to differences between the instruments, even if they are the same type of brand and model [3]. These differences can be caused by instrument characteristics, detector characteristics, type of sample presentation (for example ATR accessory) [4, 5]. Consequently, correcting these differences is necessary and can be achieved by constructing new calibration models on each new instrument or by performing calibration transfer in order to reuse the initially developed models.

The construction of robust and valid calibration models requires a large dataset of representative street samples and model validation which is labour-intensive and not always within reach. It is not always evident to build a database with representative drug samples. Exchanging samples between laboratories is subject to legal procedures. To circumvent the need of running a large number of calibration samples and creating new models each time a new instrument is used, calibration transfer procedures can be applied [6]. Once a calibration model for a FT-MIR instrument has been developed and validated, it would be convenient if it could be transferred to another instrument [6].

A major advantage is the fact that spectra can be shared easily in networks, instead of samples. According to Workman et al [7], calibration transfer refers to the use of analytical approaches or chemometric techniques to obtain a single spectral database, and a calibration model developed with that database, for two or more instruments, with statistically retained accuracy and precision.

To the best of our knowledge, this study is the first attempt to transfer MIR models for the classification and quantification of powders. Cocaine powders can have a complex and highly variable matrix. The type, the number and the concentration of adulterants and cutting agents vary [1]. This also implicates that there is spectral contribution of the adulterant(s) and/or cutting agent(s) in the MIR spectra. Calibration transfer methods using MIR spectra are yet demonstrated for liquids such as milk [8, 9] and crude oil [10]. Transfer strategies between near-infrared (NIR) instruments [6, 11] have been commonly reported in literature for powders [12], feed materials [3, 4, 13–15] and liquids such as olive oil [15].

The aim of this study was to investigate how to transfer data between FT-MIR spectrometers of the same brand (a portable versus a bench-top). Initially, it was evaluated

if there were differences between the two FT-MIR spectrometers (same brand, hard- and software and acquisition parameters). Next, three transfer strategies were investigated based on the adjustment of predictions, spectra and calibration models, respectively.
Firstly, the prediction values were modified using bias and slope adjustments. Secondly, spectra recorded on the newly purchased bench-top FT-MIR spectrometer were adjusted and predictions obtained with the original calibration models. Thirdly, new calibration models were created with spectra of both instruments. For each approach, results are compared for both the classification and quantification of cocaine. The importance of this study is to prevent the loss of extensive databases of drug samples built with an FT-MIR instrument over several years. A successful data transfer procedure will allow transferring these in-house databases to new (hand-held or bench top) devices.

Material and methods

Mid-infrared instruments

Two FT-MIR spectrometers (abbreviated respectively as portable (P) and bench-top instrument (BT)) with a single reflection diamond crystal ATR accessory with pressure applicator (Bruker Corporation, Ettlingen, Germany) were used.
Both instruments are FT using the same resolution (4 cm^{-1}), wavenumber range (4000-500 cm^{-1}) and average number of scans (24). The measurements were obtained in reflection mode and spectral intensity expressed as absorbance. Prior to analysis, all samples were homogenized with a mortar and pestle.

Reference analyses

The identification and quantification of the samples were performed at the drugs laboratory of the National Institute of Criminalistics and Criminology (NICC) using accredited methods (GC-MS and GC-FID) as earlier described [1].

Datasets

Table 1 gives an overview of the four main datasets (S1 to S4) used. Of each dataset (except for S2), subsets were created for classification (C) and quantification (Q).
The original portable P dataset (S1, n=515) included 378 adulterated powders with different amounts of cocaine and 137 powders without cocaine, collected from several seizures between 2013 and 2015. This original dataset S1 was only recorded on instrument P and was used to build different calibration models using chromatographic data as a reference for cocaine [1]. SVM discriminant analysis (SVM-DA) classification models were constructed (using S1C**P** subset) to distinguish cocaine powders from cocaine-free powders. SVM regression (SVMR) quantification models were constructed (using S1Q**P** subset) to quantify

cocaine in samples that were classified as 'cocaine positive' by the SVM-DA classification model.

The second dataset (S2, n=114) consisted of new representative cocaine samples that were measured on both instruments P and BT. S2Q**P** and S2Q**BT** subsets were used as standardization dataset for the transfer trial.

The third dataset (S3, n=291) consisted of representative cocaine samples that were only measured on instrument BT. S3 was used as calibration dataset for the construction of a mixed instrument model (consisting of spectra of instrument P and BT). As for dataset S1, S3 consisted of two subsets, one for classification (using S3C**BT** subset) and one for quantification (using S3Q**BT** subset).

The test dataset (S4, n=277) consisted of 100 drug samples without cocaine and 177 cocaine samples that were measured on the new instrument BT. S4 was used as test dataset for the evaluation of the different transfer strategies. As for dataset S1 and S3, S4 consisted of two subsets, one for classification (using S4C**BT** subset) and one for quantification (using S4Q**BT** subset).

Comparison and evaluation of the instruments P and BT

The spectra of instrument BT (1715 data points) were interpolated to 2440 data points (instrument P) using a spline function (MATLAB 2017b, The MathWorks Inc., Natick, Massachusetts, United States) due to differences in the number of data points. According to the company this difference in data points can be explained by a change of the high folding limit in the OPUS software version 7.2 in combination with the latest firmware. Consequently, this results in less data points in the current measured range after FT.

Subsequently for the comparison of the two instruments P and BT, the spectral differences between the two were evaluated using the S2Q dataset. Correlation coefficients between the wavenumbers were calculated using Microsoft Excel. Principal component analysis (PCA) was performed to explore the data of both instruments P and BT. The projections of the samples on the PCs are called the scores. The clustering of the scores can be considered as a similarity indication of samples [16]. Hotelling's T^2 and Q residuals were used to evaluate the distribution and differences of the samples. The original SVM-DA classification model (S1CP samples) and the original SVMR quantification model (S1QP samples), initially built on instrument P, were then applied to predict the uncorrected spectra.

Transfer methodology

The first strategy consisted of adjusting predictions using slope and intercept correction [7].

For the second strategy, piecewise direct standardization (PDS with window 3, SOLO version 8.7, PLS Toolbox, Eigenvector Research Inc., Manson, WA, USA) was used to match spectra of instrument BT (also called the slave instrument in literature) to spectra of instrument P (also called the master instrument in literature) [9]. For constructing the PDS model, the S2

samples (identical samples measured on each instrument) were used and the spectral difference was calculated. To evaluate the PDS method, the S4 samples were predicted by the original SVM models before and after PDS transformation.
As third strategy, a mixed instrument model, consisting of spectra of both instruments P and BT, was constructed and evaluated (table 2, model P+BT). This so called model updating blends samples measured on multiple instruments into a single calibration model [7]. To determine the minimum number of samples needed for the slope/intercept correction and mixed instrument model, the Kennard-Stone (KS) algorithm [17] was used.

For the chemometric analyses, all the calibration models were developed using the SVM algorithm (SOLO version 8.7, PLS Toolbox, Eigenvector Research Inc., Manson, WA, USA) with SNV-processed spectra and cross-validations with five random subsets and one iteration.
For the evaluation, the root mean squared error of calibration (RMSEC), the root mean squared error of cross validation (RMSECV), the root mean squared error of prediction (RMSEP), the standard error of prediction (SEP; the RMSEP corrected for bias), the coefficients of determination (R^2) and the bias were calculated.

To evaluate the inherent model errors on a single instrument (RMSEC and RMSECV), for each dataset separately or combined, SVMR models were constructed (table 2, M1 to M7). Transfer results can not be better than these intrinsic errors.

Results and discussion

Comparison between the FT-MIR instruments P and BT

First, the mean raw spectra of the S2 samples (measured on both instruments P and BT) were compared after interpolation of the wavenumbers (x-axis alignment). It can be observed that the spectral profile as well as the infrared bands position are similar for both instruments, which is visualized by the mean spectrum on figure 1. The vertical lines represent the main characteristic cocaine absorbance bands[1]. In this figure also the difference spectrum (blue continuous line) between the mean spectra (green line instrument P and red line instrument BT) is shown. Despite of the similarities in acquisition settings between the two instruments of the same type and brand, the S2 mean spectra clearly differed in intensities. Comparing the intensities of instrument P in relation to instrument BT over the full spectrum, the ratio ranged between 0.49 and 0.91.

To check whether these differences have an impact on the classification and quantification of samples using the original SVM models [1], these models were applied as such, without performing a correction of the spectra or models.

The original SVM models built on instrument P were applied to all newly recorded (uncorrected) spectra of instrument BT (n=682; S2Q**BT**, S3Q**BT** and S4C**BT**).
The original SVM classification model (SVM-DA, model built using the S1C**P** samples of instrument P) correctly predicted the presence of cocaine in these samples. The SVM classification model showed a high sensitivity, specificity and efficiency (100%).
It can be concluded that the spectral differences do not influence the classification for the tested datasets (S2Q**BT**, S3Q**BT** and S4C**BT**).

Next, the original SVM quantification model (SVMR, model built using the S1Q**P** samples of instrument P) was used to determine cocaine concentration. Table 3 summarizes the performance results with the original SVMR cocaine model without correction. Compared to the results of the original published model [1] (RMSEP = 6.27% and R^2 = 0.92), the prediction results of the S2Q**P** dataset on instrument P were in agreement (RMSEP = 6.77% and R^2 = 0.89) (table 3). As can be observed in table 3, the RMSEP and bias are higher for samples (S2Q**BT**, S3Q**BT** and S4Q**BT**) measured with instrument BT.

To conclude, for instrument P the prediction results of S2Q**P** were comparable with the originally published results [1]. The spectral variations between the two instruments make the original SVMR model, developed on instrument P, not suitable for predicting new samples as such (e.g. without correction) measured on instrument BT.

In order to be able to perform spectral transfer methods, high correlations at each wavelength between the two instruments P and BT are required. The overall spectral correlations between the S2Q spectra of the two instruments were high (R^2 > 0.9) after SNV pre-processing. Therefore, transfer strategies can be applied.

Transfer strategies

PCA was performed to assess whether the new samples measured with instruments P and BT (S2Q**P** and S2Q**BT**) lie within the original calibration dataset S1, collected on instrument P. Figure 2 shows that the calibration dataset S1 covered mostly the space of the new datasets, but spectral variability in the scores of S2Q**P** and S2Q**BT** was noticed. Moreover, more variation is observed within the S2QP dataset (red diamonds figure 3). Outliers (samples outside the 95% interval, see circle figure 3) were not excluded and represent cocaine samples with cocaine concentrations below 40%.

Three transfer strategies were tested: 1) correction of slope/intercept, 2) correction of spectra and 3) development of a new mixed instrument model.

1) Correction of slope/intercept

The first option consisted of a slope/intercept correction of the predictions. Linear regression was performed between the cocaine predictions of the S2Q**P** (instrument P) and S2Q**BT** dataset (instrument BT). The resulting slope and intercept were used to correct the predictions of instrument BT (S2Q**BT**).
As shown in figure 4, there is a linear correlation between the S2Q**P** and S2Q**BT** dataset (R^2 = 0.90). Therefore, the predictions of instrument BT were corrected, based on the equation of the S2Q dataset (see figure 4). Using the S4Q**BT** dataset as a test set, it was observed that the predictions improved: RMSEP decreased from 8.86% to 6.37% and bias decreased significantly from -6.27 to -0.32.

Slope and intercept correction of the predicted data from a secondary instrument is an easy, cost-effective approach but its simplicity could led to errors when performing on a small dataset and over a large concentration range [11].
Therefore, to apply this approach, it is recommended to include a minimum of samples (in this case 114 samples were used) and fulfil two requirements. First criterion, it is important to check whether the spectra fall within the calibration dataset (figure 2 and 3). This could be done by evaluating Hotelling T^2. Second criterion, the samples should be classified as 'cocaine' by the SVM-DA classification model and only then they will be quantified by the SVMR quantification model.
To determine the minimum of samples required for the slope/intercept approach, different subsets of samples (using KS selection [17]) were used. The RMSEP values were compared to those obtained by using the full S2Q dataset (n=114). Up to 20% of the S2Q samples, RMSEPs ranged between 6.51 and 9.27%. If 30% of the available spectra were included, even better results (RMSEPs 6.21%) could be achieved, suggesting that the KS-based selection enabled more accurate predictions. KS-selection enabled to reduce the number of spectra to be collected with 70% (n=35). From 40% of the S2Q samples onwards, RMSEPs and biases were comparable with full calibration (see supplemental table S1).

2) Correction of spectra (PDS)

To match all new spectra recorded on the slave instrument BT to the master instrument P, a PDS transfer model was tested using the S2Q dataset. Before standardization, the spectral difference between S2Q**P** and S2Q**BT** was 0.4669. After SNV correction and standardization this spectral difference was reduced to 0.1202. The final step consisted of applying the PDS model on all the spectra from instrument BT to correct these spectra on the wavenumber (x-) axis and the intensity (y-) axis.

Table 4 shows a summary of the results before and after applying PDS. To conclude, after applying PDS the RMSEP, bias and R^2 (except for S4Q**BT**) improved for all datasets. PDS did not correct for all the differences. RMSEP's are reduced but significant biases remained (except for S3Q**BT** and S4Q**BT**).

3) Creation of a mixed instrument model

A mixed SVMR model with spectra of the two instruments P and BT was constructed. This mixed model is a merge of S1QP, S2QP, S2QBT and S3QBT samples (n=813) and had a RMSEC of 4.47% (R^2 of 0.96) and RMSECV of 6.20% (R^2 of 0.91).
To evaluate this new mixed model, the test dataset S4Q**BT** was predicted. A RMSEP of 5.08%, a bias of 1.61 and a R^2 of 0.93 were obtained. It was noticed that the addition of spectra from the second instrument BT did not increase the RMSECV's of instrument P and BT (see table 2, models M1 to M7).
For constructing a mixed model, it is necessary to measure samples on the new instrument. In this case, the dataset of the mixed models (instrument P + BT) consisted of a large number of cocaine samples (n=813). To evaluate how many samples are needed to construct a mixed model, the KS algorithm [17] was used to select subsets of S2Q**P**, S2Q**BT** and S3Q**BT** samples. Subsequently, each KS subset was added to the S1Q**P** dataset (n=378) and a mixed model was then constructed. These mixed models were again evaluated by the S4Q**BT** dataset (table S2 supplemental). When building a mixed model with S1Q**P** and a very small instrument BT calibration subset (up to 10% of the S2Q**P**, S2Q**BT** and 3Q**BT** samples, n=44), the model performance for the S4Q**BT** dataset (RMSEP of 5.27%, bias of 0.95 and R^2 of 0.92) was comparable to a full recalibration (RMSEP of 5.08%, bias of 1.61 and R^2 of 0.93). From 20% of the S2Q**P**, S2Q**BT** and 3Q**BT** samples onwards, similar results (table S2 supplemental, RMSEPs between 5.28 and 5.44%) could be achieved, suggesting that the KS-method selected the most representative spectra.

To conclude, the results of the S4Q**BT** dataset using the KS sample reduction for all three transfer methods are summarized in table 5. Overall, the results of the slope/intercept approach and the PDS approach were comparable with RMSEPs ranging between 6.37% and 6.45%. The mixed model approach performed best with a RMSEP of 5.08%. Compared to the PDS approach, the approach of slope/intercept correction and mixed instrument model is interesting since it is not always possible to do parallel measurements for example in the case of instrument failure (fire,…).

Conclusion

Three calibration transfer strategies between a bench-top and a portable FT-MIR instrument were evaluated. All three strategies improved the prediction of cocaine concentrations in comparison with uncorrected data. The construction of a new mixed SVMR model for the two instruments resulted in the best performance, compared to the two other strategies based on slope/intercept correction and spectral standardization (PDS). Furthermore, the number of spectra required on the secondary instrument for the calibration transfer could be reduced with 90% applying the Kennard-Stone sample reduction approach. Taking into account the daily workload of a forensic lab, the proposed strategy enabled accurate predictions and allowed to reduce the time and costs of the transfer. In the future, the implications regarding transferring between different brands (with different sampling tools) can be investigated. It offers opportunities to exchange data within a network of forensic laboratories.

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Table 5: Summary of the S4Q**BT** results applying three transfer strategies and Kennard-Stone sample selection.

	Before transfer	**After transfer**		
	No correction[(1)]	**Slope/intercept correction**[(2)]	**PDS-correction**[(3)]	**Mixed instrument model**[(4)]
RMSEP	8.86	6.21	6.45	5.27
bias	-6.27***	-0.69	-0.88	0.95
R^2	0.89	/	0.89	0.92

[(1)]application of calibration model S1QP [1]; [(2)]predictions BT corrected to P using subset of S2Q by KS (n=35); [(3)]spectra BT transformed to P using S2Q (n=114); [(4)]combined spectra of P and BT using S1QP (n=378) and subsets of S2QP, S2QBT and S3QBT by KS (n=44).

Table 1: Characteristics of the datasets used.

ID DATASET	ID SUBSET	N spectra	Cocaine concentration range (w/w %)	Median cocaine concentration (w/w %)	Period of analysis (month/year)
S1 Calibration dataset [1]	S1CP S1QP	515 378	4-100	76	01/2013– 07/2015
S2 Standardization dataset	S2QP S2QBT	114	9-100	70	01/2016– 02/2017
S3 Calibration dataset (model updating)	S3CBT S3QBT	291 207	9-100	83	01/2016– 02/2017
S4 Test dataset	S4CBT S4QBT	277 177	20-100	87	10/2017– 08/2018

Legend: S = dataset; C = classification; Q = quantification; P = portable; BT = bench-top.

Table 2: Overview of the constructed SVMR models to quantify cocaine content.

Model	**Dataset**	**N spectra**	**RMSEC**	**R^2 C**	**RMSECV**	**R^2 CV**
M1 [1]	S1Q**P**	378	4.12	0.97	6.08	0.93
M2	S2Q**P**	114	4.49	0.94	6.26	0.88
M3	S1Q**P**+S2Q**P**	492	5.57	0.93	6.67	0.90
M4	S2Q**BT**	114	1.43	0.99	5.73	0.90
M5	S3Q**BT**	207	5.94	0.92	7.63	0.87
M6	S4Q**BT**	177	3.21	0.97	4.68	0.93
M7	S2Q**BT**+S3Q**BT**	321	2.66	0.98	5.92	0.92

Table 3: Summary of the quantification results of the datasets S1Q to S4Q predicted with the original SVMR cocaine model [1] without correction.

	Instrument P		**Instrument BT**		
	S1QP [1]	**S2QP**	**S2QBT**	**S3QBT**	**S4QBT**
RMSEP	6.27	6.77	8.72	10.76	8.86
bias	0.26	2.72***	-3.45***	-6.19***	-6.27***
SEP	6.27	6.20	8.00	8.80	6.25
R^2	0.92	0.89	0.81	0.85	0.89

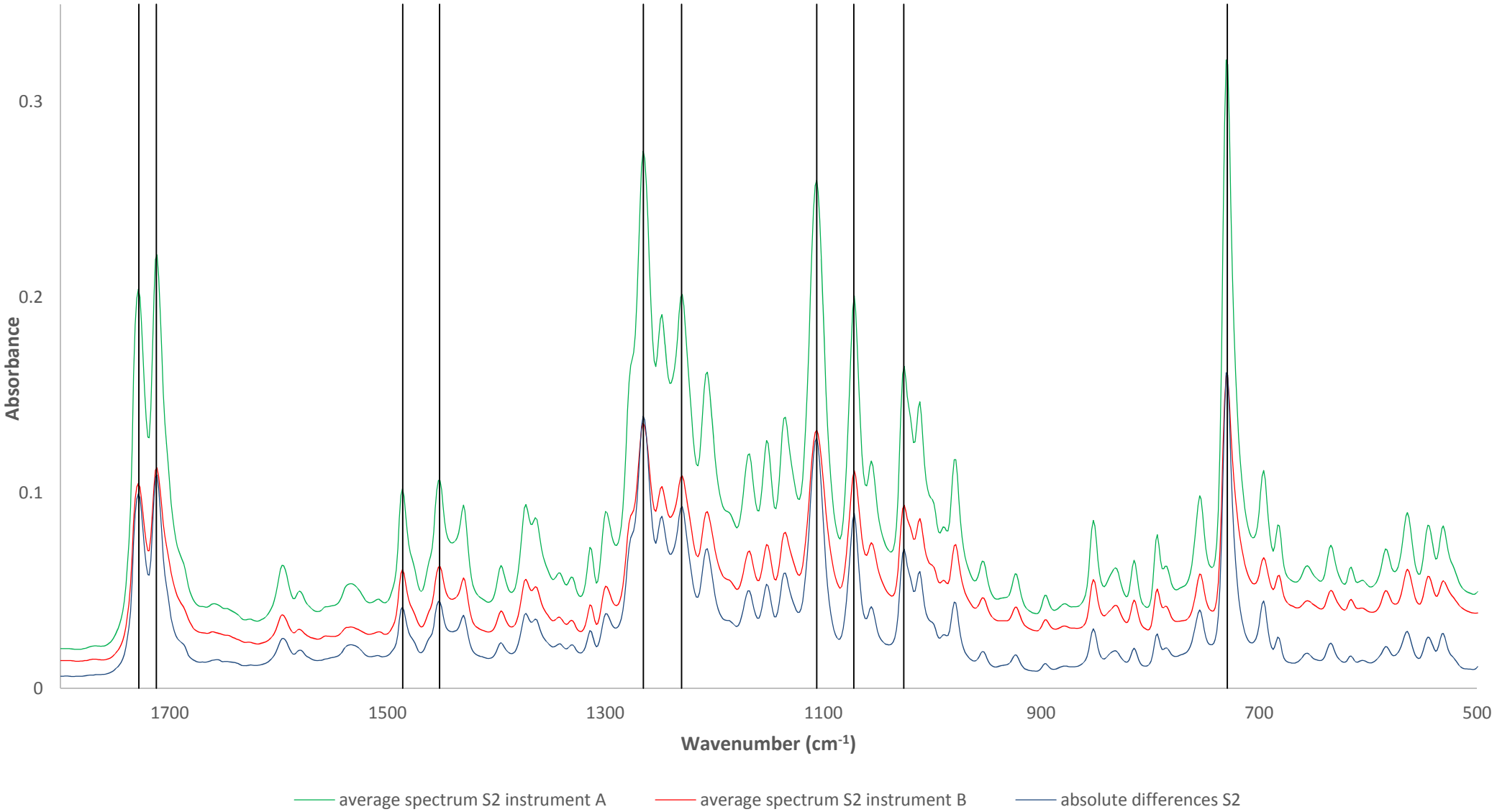
***significant biases: α=0.01

Table 4: Summary of the quantification results of the datasets S2Q**BT** to S4Q**BT** predicted with the original SVMR cocaine model before and after PDS-correction of the spectra.

	S2QBT		**S3QBT**		**S4QBT**	
	raw	**PDS-corrected**	**raw**	**PDS-corrected**	**raw**	**PDS-corrected**
RMSEP	8.72	7.95	10.76	7.97	8.86	6.45
bias	-3.45***	2.72***	-6.19***	-1.03	-6.27***	-0.88
SEP	8.00	7.47	8.80	7.91	6.25	6.39
R^2	0.81	0.84	0.85	0.88	0.89	0.89

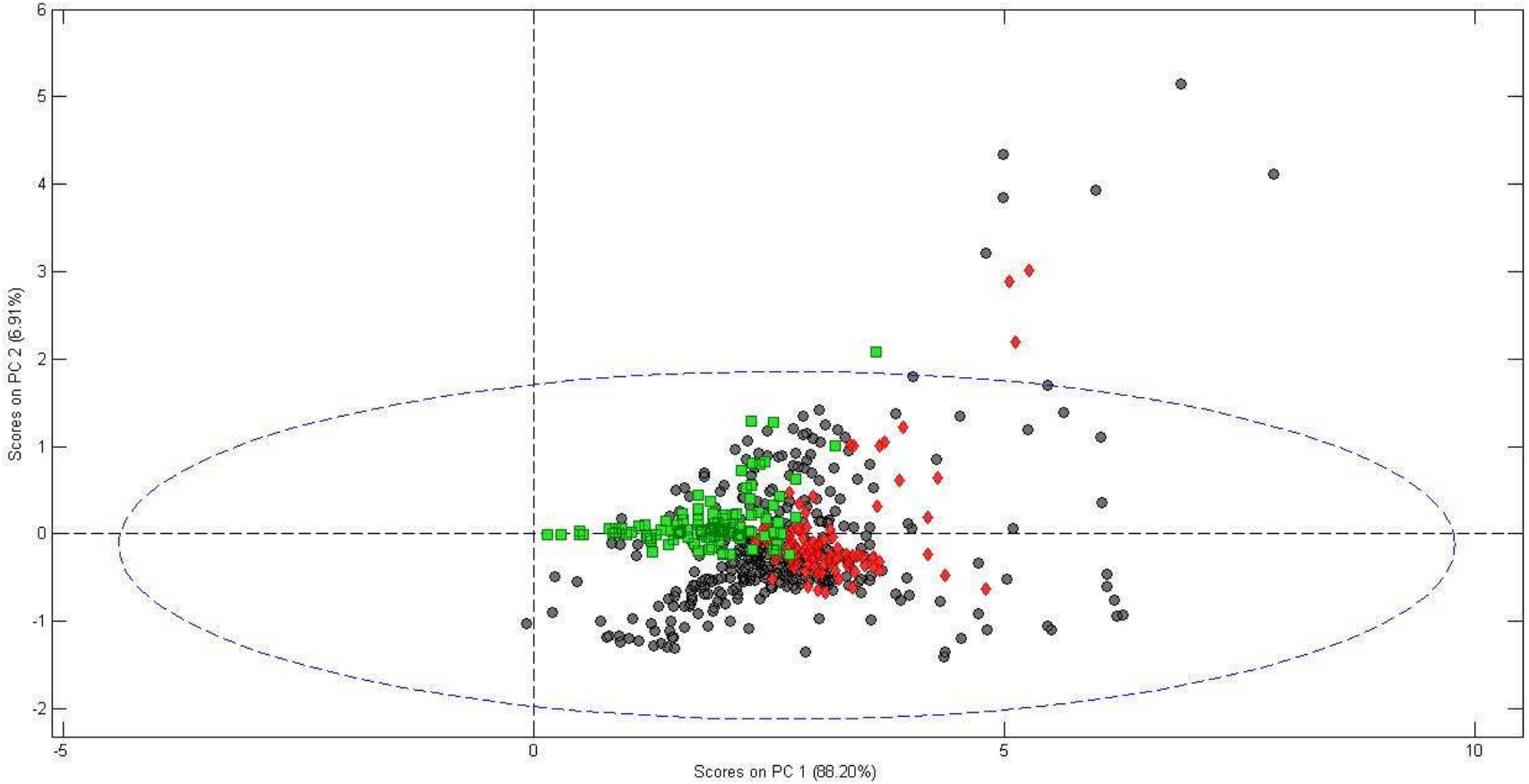
***significance 0.01

Figure 1. Comparison of the standardization dataset (S2Q) measured on instrument P (average spectrum; green line) and instrument BT (average spectrum; red line) after x-axis alignment in the fingerprint region (1800-500 cm^{-1}).



Legend: Black vertical lines mark the main vibrational bands of cocaine hydrochloride; The absolute differences between the S2QP and S2QBT spectra are presented by a blue line.

Figure 2. Score plot of the raw datasets S1QP and S2Q (instruments P and BT).



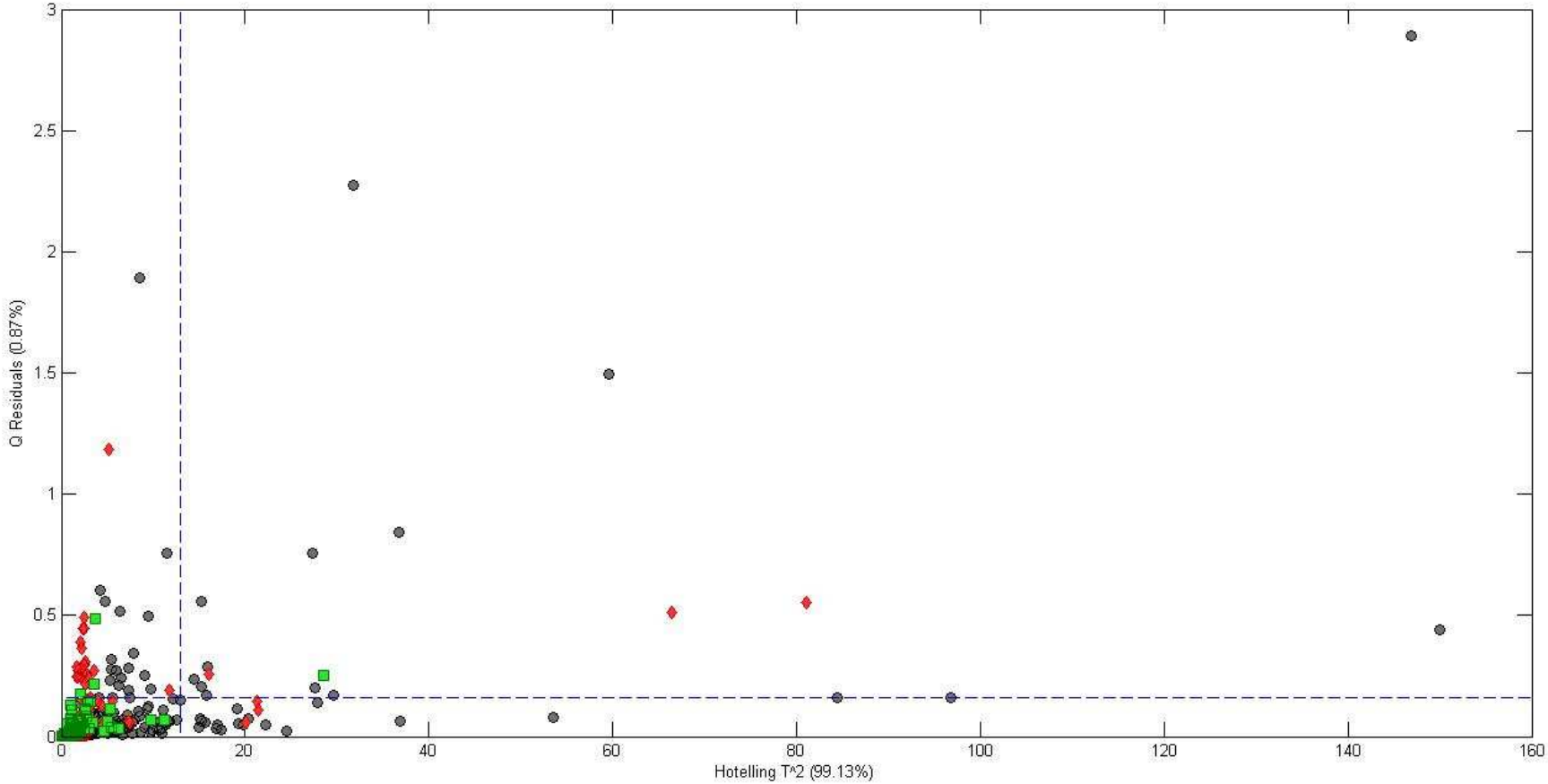
Legend:

PC1: principal component 1
PC2: principal component 2

black circles: dataset of instrument P (S1QP)
red diamonds: dataset of instrument P (S2QP)
green squares: dataset of instrument BT (S2QBT)

ellipse: 95% CI interval

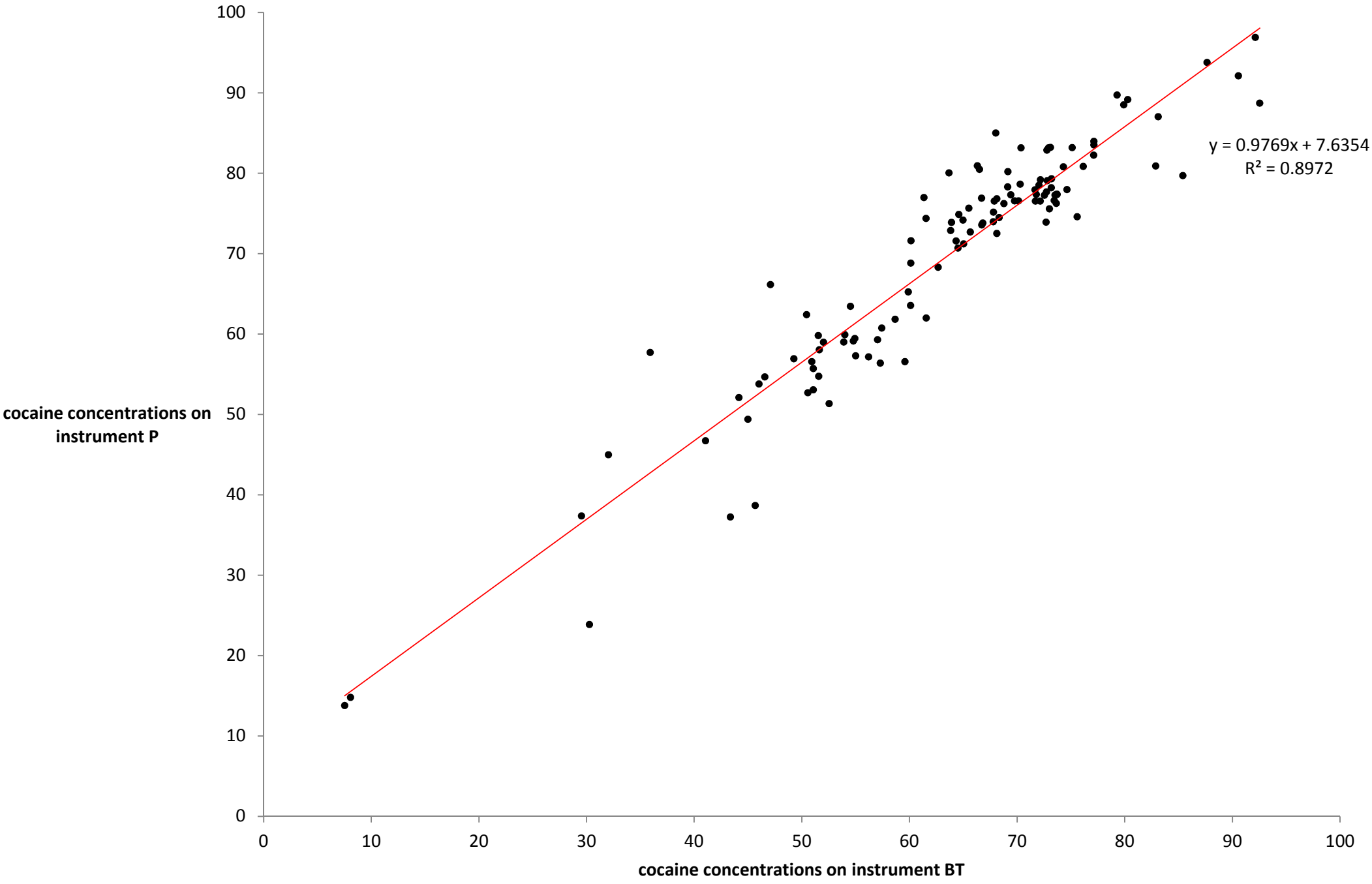
Figure 3. Q residuals versus Hotelling T^2 reduced.



Legend:

black circles: dataset of S1QP
red diamonds: dataset of S2QP
green squares: dataset of S2QBT

Figure 4. SVMR predicted cocaine concentrations on instrument P in relation to SVMR predicted cocaine concentrations on instrument BT for the S2Q dataset.



Highlights

- How to prevent data loss when purchasing a new MIR instrument?
- Calibration transfer of MIR spectra of powders between a portable and bench-top instrument is presented.
- Comparison of three transfer strategies.
- Best prediction results were obtained using mixed model approach.
- The approach offers opportunities to exchange data within a network of forensic laboratories using other FT-MIR spectrometers.