

Wavelength selection and probe design for the customisation of micro-spectrometers

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The rapid development in the field of micro-spectrometers has made cheap spectroscopic sensors a reality (see, for example, Figure 1). However, grating-based micro-spectrometers suffer from comparatively poor performance in comparison with conventional laboratory equipment. Not only is the wavelength resolution substantially impaired, but often the dynamic range is reduced and the noise levels are significantly higher.

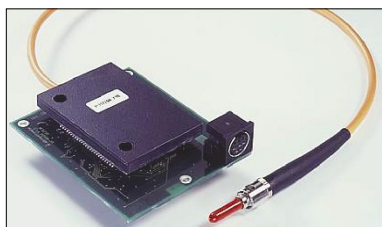


Figure 1. An example of a microspectrometer, the NIR1750 reproduced with permission STEAG microParts, Dortmund, Germany.

So why use them? First, they can be significantly cheaper than conventional spectrometers and have the ability to be used in groups of instruments with different characteristics, controlled by a single personal computer. Second, these systems are perfectly suited for use with fibre-optic sensor probes allowing mixing and matching of off-the-shelf components to respond flexibly to particular analytical needs.

In this article we would like to investigate a further possibility presented by the advances in this technology and that is the design of cheap, dedicated systems customised for a particular analytical task. By not trying to mimic the flexibility of present analytical laboratory equipment, an attempt which is

doomed to failure, but by concentrating on the strengths of the new technologies it is possible to produce powerful, dedicated, cheap spectroscopic sensors.

Wavelength selection

The key to designing such systems is a correct determination of which wavelengths are really required to carry out the desired analysis and which provide no useful analytical information. Once this information is available it is possible, for example, to design gratings for spectrometers which only deliver the required wavelength range to the detector arrays, thus optimising the available limited spectral resolution. In order to carry out such developments effectively, it is important to ensure that the system which is to be monitored is well understood. An example of such a development from the Institute of Spectrochemistry involved the measurement initially of a large number of samples using research grade laboratory spectrometers to obtain reference data covering as much of the sample variance as possible. The samples, in this case adulterated extra virgin olive oils, delivered excellent spectra with virtually no obvious differences in the observed bands. The aim of the initial studies was to obtain a feeling for how much the vastly differing geographical origins of the oils affected their Raman and infrared spectra in comparison to variations caused by the low levels (between 1% and 10%) of the adulterant vegetable oils. The data sets were then subjected to a multivariate calibration based on the reference data, yielding good standard errors of prediction of sub 2% adulterant.^{1,2}

This approach is fine for a reference laboratory but is too expensive in terms

of capital equipment and required manpower for application in a front-end customs lab where large numbers of samples would need to be tested in quick succession. Here a red light/green light spectroscopic sensor would suffice if it could be proven to be reliable in its decision-making and robust enough for use by non-technical personnel. Those samples then flagged as questionable could then be forwarded to the reference laboratories for further analysis.

The PLS calibrations used by us to analyse the results from the research grade spectrometers can be used to determine the optimal number of PLS factors to be taken into consideration and, in a second step, to select the wavelengths for achieving a significantly more robust PLS calibration model than obtained using full spectrum data. A preselection of a suitable wavelength interval is usually done by inspection of the covariance vector of the spectral variables and the response variable (also called "property correlation spectrum"). A calibration model derived in this way could be considered for a dedicated olive oil quality sensor.

The procedure chosen for this wavelength selection involved studying the contribution of the individual spectral variables to the calibration and searching for those providing the most weight in absolute figures for the calibration. A selection procedure based on significance testing of the regression coefficients, previously developed by Westad and Martens,³ was covered in the previous column by A.M.C. Davies.⁴ Our method yields similar results, but we selected wavelengths using the regression coefficients which provided pairwise the maximal and minimal weightings to the calibration, starting with the most influential pairs.⁵ This procedure can be regarded as similar to finding the best peak height and

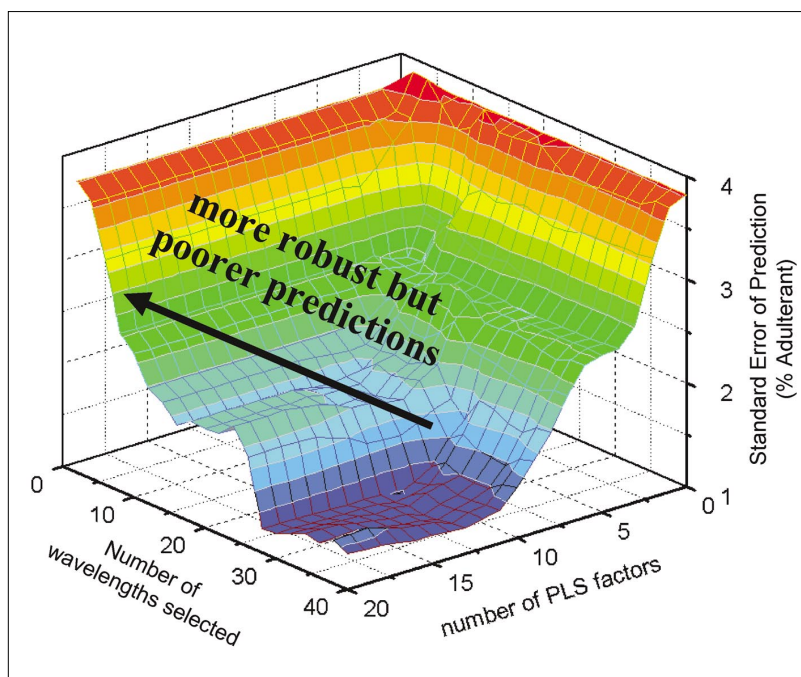


Figure 2. Effect of reducing the number of spectroscopic variables on the predictive quality of the calibration.

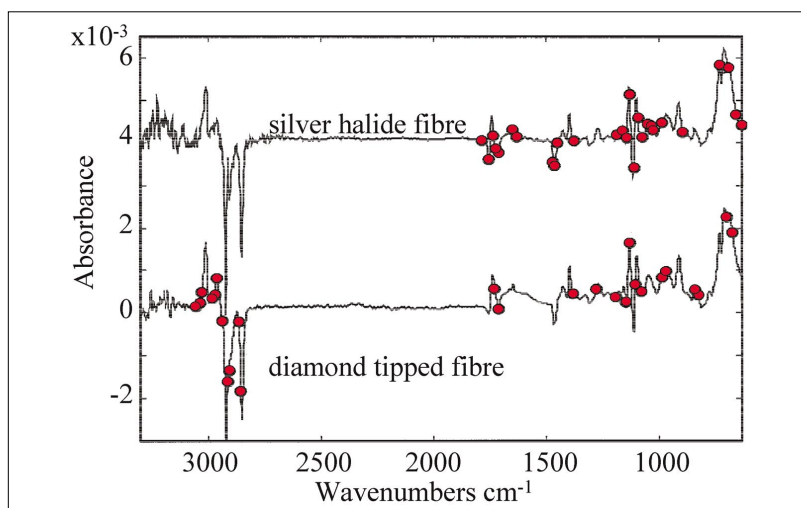


Figure 3. Location of the selected wavelengths for the optimal calibration (red points) for two different optical fibre probes and olive oil adulteration samples.

baseline point in a classical “univariate” approach. Our strategy provides a more parsimonious calibration model with respect to the number of spectral variables than suggested by the significance testing method. In Figure 2 the prediction error from leave-one-out cross-validations is plotted for various numbers of PLS factors where the number of wavelengths used for calibration increased from 2 pairwise to 40. During the model testing, it is not possible to calculate predictions using more PLS factors than wavelengths available, but for ease of presentation the curves in Figure 2 are extended to the axis in such cases. The optimal

number of wavelengths and PLS factors for the calibration can be found by locating the minimum (or by F-testing) in the surface generated by this method (see Figure 2).

This may sound complicated but is in fact a relatively simple procedure to carry out and yields significant benefits with regard to calibration robustness and, of course, the information we require for parameterising our customised microspectrometer.

In Figure 3 an example is shown plotting the property correlation spectra for the olive oil adulteration experiment with the wavelengths selected as being the best for a robust calibration

highlighted by the red circles. What is significant here is that by opting for a diamond tipped infrared ATR probe, variables come into play which were deliberately ignored in the all silver halide fibre ATR probe. This is due to the large variances observed here from the low single beam intensities arising out of the intrinsic fibre attenuation. Carrying this design criteria to its logical conclusion would then allow us to opt for a grating optimised for 500–2000 cm^{-1} if we were using the silver halide probe but would need to expand the range, thereby losing spectral resolution if, possibly for reasons of mechanical robustness such as in industrial process analysis, a diamond tipped probe was required.

Figure 3 is still relatively complicated to follow but the same data treatment has been applied by us to the problem of gas analysis in sulphur hexafluoride filled high-tension switchgear monitoring. By moving from liquid to gas analysis we start dealing with significantly narrower linewidths which can be spectrally resolved down to the baseline or at least in this case resolved features on a broad background signal. In Figure 4, taken from the current thesis of one of the authors (RK), one of the toxic by-products monitored following a stress experiment on SF_6 gas can be found to be calibrated successfully using only four wavelengths and the figure also clearly shows the algorithm has selected maxima and minima for the two bands in the spectral range observed. If we wished to consider building a microspectrometer specifically to analyse for such components, then the new quantum cascade lasers could certainly be called into play as a significantly better light source for the mid-infrared analysis and by stepping the small-banded lasers on and off the selected wavelengths the absorption data could be collected without the need for the problematic dispersive element (grating) (see also Reference 6).

Probe designs

The key to being able to make these micro-spectrometers really useful is the range of sampling probes which are now available. As we have already shown in Figure 3, diamond tipped optical fibre probes can be attached to the spectrometers capable of withstanding the chemically aggressive high temperature and high pressure environments often found in industrial chemical processes. This ability is dependent on the method by which the diamond ATR crystal has been bonded to the optical fibres themselves—glued tips not being as inert or physically robust.

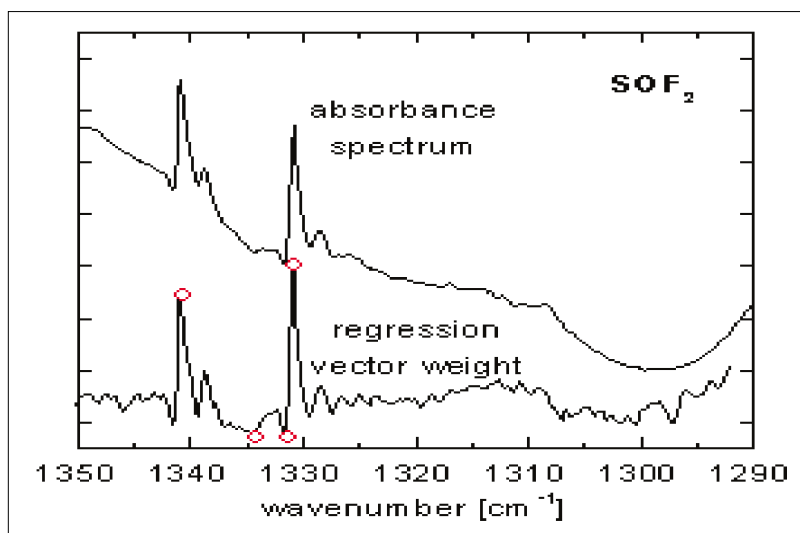


Figure 4. SOF_2 optical wavelength selection, upper trace is the spectrum and the lower trace the regression vector with the selected wavelengths shown as red circles.



Figure 5. Exchangeable tips for silver halide IR fibre probes.

If the application requires better optical throughput then we have designed fibre probes with exchangeable heads allowing for the possibility of wear and

tear of the probe but building in a simple way to deal with this problem without having to renew the entire optical probe (Figure 5).

Another optical fibre-coupled device successfully tested recently has been coupling conventional mid-infrared light pipes to novel silver halide optical fibres for use as micro-cuvettes in trace gas analysis (Figure 6). We have been able to test optical pathlengths up to 18 cm.

Optical fibre probes offer themselves to multiplexing techniques whereby a number of separate probe heads are connected to a single spectrometer. This route can bring problems with the additional loss of intensity due to the presence of the multiplexer in the optical train and so the advantages should always be weighed up against the inherent disadvantages. Finally, it

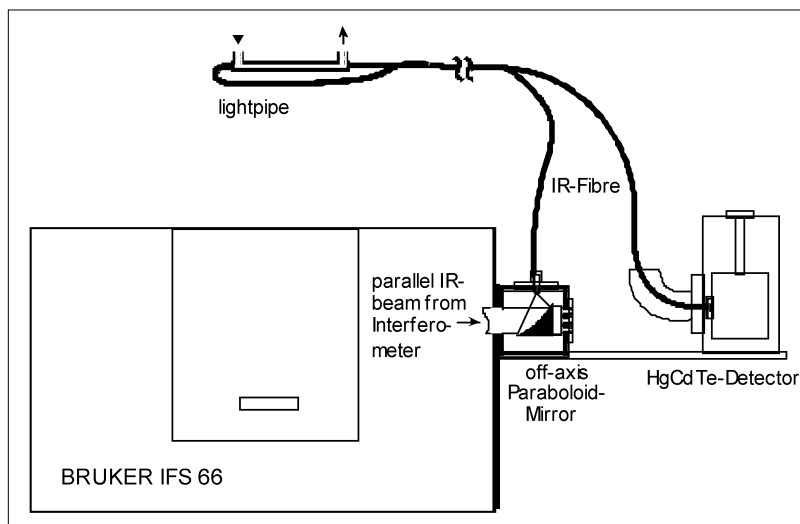


Figure 6. Conventional infrared lightpipe assembly connected through novel infrared fibres to act as a micro-trace gas analysis cell.

should be mentioned that coupling can also be conveniently done to small volume Fourier transform spectrometers such as introduced by Egevskeya.⁷

Conclusions

These examples try to show some of the possibilities slowly becoming available for the construction of dedicated micro-spectrometer systems making use of new optical-fibre technology and excitation sources. Technologies which can really take off when combined with intelligent use of chemometrics including wavelength selection techniques.

References

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