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FOURIER TRANSFORM - INFRARED SPECTROPHOTOMETER FOR AIR MONITORING

G. Andria(1), *A. Lay-Ekuakille*(2)

(1)Dipartimento di Elettrotecnica ed Elettronica, Politecnico di Bari, Via Orabona 4, 70125 Bari (Italy)
(2) Dipartimento d'Ingegneria dell'Innovazione, Università di Lecce, Via Arnesano, 73100 Lecce (Italy)
Phone +39.0832.320226 - Fax +39.0832.325369, e-mail: aime.lay.ekuakille@unile.it

Abstract − Compounds can be classified by infrared spectroscopy through the variation of their transmittance, reflectance or emittance with frequency. At the present time, measurement of the transmittance spectrum of a sample is the usual means of identifying a material; reflectance spectroscopy is used infrequently while emission spectra are hardly ever measured. One of the principal reasons for the unpopularity of infrared emission spectroscopy is the experimental difficulties involved, especially when the sample is only able to be heated to very slightly above room temperature. In this case the energy at the detector is very low compared to the energy from the incadescent sources used in absorption or reflection spectroscopy, so that instrumental sensitivity limited the applications of the technique until the development of Fourier transform spectroscopy. In this paper we outline the application of virtual commands, by means of a pannel, to be applied in order to broad the use of a FT-IR spectrophotometer to characterize compounds.

Keywords: FT-IR spectrophotometer, air monitoring, interreflection error

1. THEORETICAL FOUNDATIONS

There are others difficulties besides sensitivity encountered in the measurement of infrared emission spectra. The radiation emitted by, or reflected from, the surroundings can be of comparable intensity to the emission from the sample when the temperature of the sample is low, and some means of discriminating against this spurious radiation often has to be applied. Temperature gradients across the sample can lead to spectra that are difficult to interpret. For quantitative analysis by infrared emission spectroscopy [1], the emissivity spectrum, $\varepsilon(\bar{v})$, of the sample must be determined. Methods of measuring the emissivity of a sample in a laboratory are known. For any sample, the sum of its transmittance, $T(\bar{v})$, reflectance, $\rho(\bar{v})$, and emissivity, $\varepsilon(\bar{v})$, at any frequency, ν, is approximately equal to unity:

$$T(\bar{v}) + \rho(\bar{v}) + \varepsilon(\bar{v}) = 1 \qquad (1)$$

Since the reflectance of most samples with discrete emission spectra is low, to good approximation we have that

$$\varepsilon(\bar{v}) = 1 - T(\bar{v}) \qquad (2)$$

The absorbance of a sample, $A(\bar{v})$, related to the absorptivity, $a(\bar{v})$, pathlength, *b*, and concentration, *c*, by the Beer-Lambert law:

$$A(\bar{v}) = -\log_{10} T(\bar{v}) = a(\bar{v}).b.c \qquad (3)$$

so that the emissivity of the sample is related to its concentration by

$$c = \frac{-\log_{10}\left\{1 - \varepsilon(\bar{v})\right\}}{a(\bar{v}).b} \qquad (4)$$

or $$\varepsilon(\bar{v}) = 1 - 10^{-a(\bar{v}).b.c} \qquad (5)$$

Altough this is a good approximation for gases, many condensed phase samples are held on a low emissivity support, such as metals of light reflectance.

2. ADVANTAGE SURVEY

The heart of a FT-IR spectrophotometer (FT-IRS) is an interferometer, that has several basic advantages over a classical dispersive instrument. Some of These advantages are [2]:

- all source wavelenghts are measured simultaneously in an interferometer, whereas in a dispersive spectrophotometer they are measured successively. A complete spectrum can be collected very rapidly and many scans can be averaged in the time taken for a single scan of a dispersive spectrophotometer;
- for the same resolution, the energy throughput in an interferometer can be higher than in dispersive spectrophotometer, where it is restricted by the slits. In combination with the multiplex advantage, this leads to one of the most important features of an FT-IR spectrophotometer: the ability to achieve the same signal-to-noise ratio as dispersive instrument in a much shorter time.

As the IR spectrum is the feature of intensity function in the frequency domain, so the interferogram is the representation of the same intensity in the time domain (or spatial domain if it is referred to the uniform motion of mirror). Indicating with x the variable of interferometer scanning (it is expressed in space or time units), with ν the frequency of radiation emitted by the source, with $S(\nu)$ the spectrum function, and with $T(x)$ the interferogram function, thus, the Fourier transform is given by the relationship:

$$S(\nu) = \int_{-\infty}^{+\infty} T(x)(\cos 2\pi \nu x - i sen 2\pi \nu x)dx \qquad (5)$$

The inverse transformation, from interferogram to spectrum, is obtained by means of the function called Fourier inverse transformation and is expressed by the following equation:

$$T(x) = \int_{-\infty}^{+\infty} S(\nu)(\cos 2\pi \nu x - i sen 2\pi \nu x)dx \qquad (6)$$

Since the transformation operation is executed by a computer, first of all, it is necessary to sample the interferogram, by converting it into a succession of discrete values. In this context, to act the operation, function described by (5) is only a sum. Moreover, since it is not possible to extend such sum between - ∞ and + ∞ for instrumental reason, it requires to cut off the signal assigned to processing: that creates anomalies in the interferogram that are cancelled with the use of adequate corrective functions.

3. SYSTEM ARCHITECTURE

There are two main limitations to FT-IRS. The first is the cutoff at short wavelengths because of the need for a transmitting substrate to act as beamsplitter as shown in Fig.1 (the transmission of fused silica falls sharply below 180 nm) and the stringent optical and mechanical tolerances required. The second limitation is the requirement for a source that remains reasonably constant in intensity over the period of the scan, because fluctuations in intensity translate into noise in the spectrum. In this paper, we take advantage of the speed, power and relative cheapness of modern computers, to build a filtering system and a remote interface (front panel) so that it is possible to guide and control the FT-IRS. In this context, it is suitable to use one instrumentation for different users.

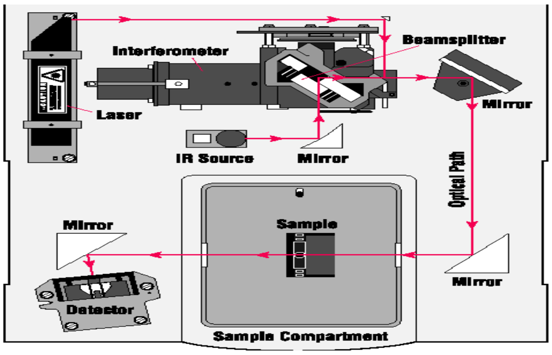

Fig. 1. FT-IRS layout

The proposed instrumental layout concerns a signal processing of a spectrum, for instance, a pollutant or another gaseous element. The spectrum is obtained from the interferogram by Fourier Transformation. This process analyzes the interferogram as the sum of a series of sine and cosine waves with discrete frequencies.

The range of frequencies used in the Fourier analysis is limited by the way in which the interferogram is stored as a series of discrete points. There must be at least two data points for each cycle if a wavelength is to be recognized correctly (the Nyquist criterion). This means that the interferogram must be mesured at intervals equal to half of the shortest wavelength from the source to be measured. Radiation at shorter wavelength may contribute to the interferogram, but will appear at the wrong place in the final spectrum. This effect is known as aliasing. The problem is avoided by filtering our shorter wavelength optically or electronically. Here, we use a digital filtering with least-squares filter. We have used this kind of filter since the aim is to find a filter that minimizes the squared error.

The sampling points for measuring the interferogram are derived from the laser signal [3]. If one data points is recorded for each cycle of the laser signal, the data poit separation is equal to the laser wavelength (in a vacuum) of 632.99 nm. The resolution in the final spectrum depends on the maximun optical path difference in the interferogram.

The Fourier transformation analyzes the interferogram as the sum of the contributions from individual wavelengths. However, the Fourier transformation is not able to distinguish wavelength properly between wavelengths that differ by less than half a cycle. So two wavenumbers $\bar{\nu}_1 - \bar{\nu}_2 = \frac{1}{2d_{\max}}$ Where $d_{\max}$ is the maximun optical path difference. A useful approximation is that two spectral features must be at least two such spacings apart to be resolved.

This means that the resolution is approximately the reciprocal of the maximun optical path difference scanned.

4. DATA PROCESSING AND ERROR DETECTION

In both qualitative and quantitative spectroscopic analysis, Fourier transfrom spectrophotometry has become the dominant technique from near infrared to the very far infrared spectral regions. This because the multiplex and throughput advantages [4] generally work in favour of FT-spectrophotometry and against grating-based spectrophotometry, leading to FT-derived spectra which have low levels of random error on their ordinate scale (often less than 0.1% transmittance or reflectance), but for which possible systematic effects have not been discussed to any significant extent. Now, however, the ongoing pressure from in-house and externally accredited Quality Assurance schemes will ensure that the study of such systematic effects is a subject area whose time has finally come. In this section we introduce our “way” to study , as a first approach , the sources of errors (quantitative systematic errors) and wether or not it is best to correct for them or to design instruments in which they are minimised [5].

In the context of FT spectrophotometry, significant ordinate error is assigned to the dependent spectral variable is less than the actual systematic error, even though the magnitude of latter may not be known or its presence even suspected. The important point is that such errors can be unexpectedly large. In a recent FT spectrometry-led round robin specimen intercomparison [6], for example, measured absorption coefficient values were found to vary by order of magnitude in the low wave number region around 10 cm^{-1}.

Such errors are not welcome participants in the measurement process, and it is important to be aware of them and to know how to allow for them.

So, how do we get such errors and what are their sources? The generic answer is surprisingly simple[7]: The source of all significant systematic error in FT spectrophotometry is the Fourier transform process itself, or rather more rigorously, our interpretation and implementation of it. In principle and according to our first simulations, FT spectrophotometry is a simple and elegant technique for spectral analysis. It is based on a simple optical configuration and a straightforward mathematical transformation.

The ideal FT-IR spectrophotometer is depended on [8] the following assumptions which are presented in a simplied form here:

- the input source is a point source, and the collimator and the anti-collimator mirrors are aberration free. This is the plane free. This is the plane wave assumption.
- there are perfect transfer optics from the source to detector;
- there is a unidirectional energy flow, source to detector;
- the source and the detector are non reflective;
- the specimen is ideal. It is homogeneous, nonscattering and the media boundaries are plane and parallel.

When a spectrophotometer is tested [9] for the errors in its ordinate scale, the net result is very difficult to interpret, because of the possible presence of a proportion of the fifty o more categories of ordinate error. It is essential to have diagnostic tests that separate out the categories of error into at least some related groups. In particular, one needs to be able to distinguish between interreflection effects and other groups of categories that are more intrinsic to the basic function of the detector system and the Fourier transform process. As a start o this problem, we can consider the use of optical filters that are of medium to high reflectance and those are of low reflectance (of only some 3-5%) like many types of common sample [10].

Filters with medium to high reflectances exaggerate the effects of interreflections for most applications and are excellent for investigating them. However, they are not suitable for calibrating the ordinate scale, as they are unrepresentative of most samples and more importantly one would want to take steps to reduce or eliminate the interreflection effects before testing the intrinsic integrity of the ordinate scale.

In this first approach of eliminating errors created by FT-IR spectrophotometer processing algorithm, we have performed signal simulation. In Fig.2 and Fig.3 we illustrate the results of signal processing of normalized spectrum (y axis) of a blackblody radiation at 1273 K under non-purged operating conditions. They leads to atmospheric absorption of water and carbon dioxide.

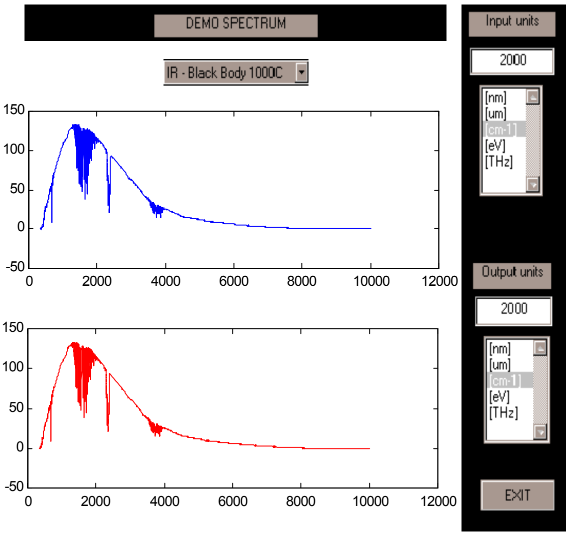

Fig. 2. Normalized spectrum versus wavenumber for 2000 inputs

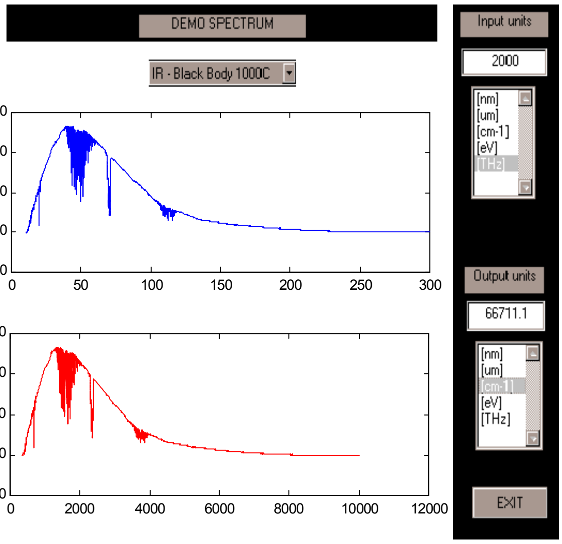

Fig. 3. Normalized spectrum versus wavenumber for 2000 inputs in different unit

Simulation data were obtained true RMS meter, blackbody radiation was modulated with mechanical chopper and the bare detector element was irradiated by known radiation flux orginating from a blackbody at 1273 1273. The detector gain is optimized for the appropriated source. From Fig. 2 and Fig.3, in further development, it will be possible to optimized the extraction of atmospheric absorption of water and carbon dioxide or other gases. In Fig. 4, a hargon spectra is illustrated; it was obtain from a post-processing of CCD system with our algorithm.

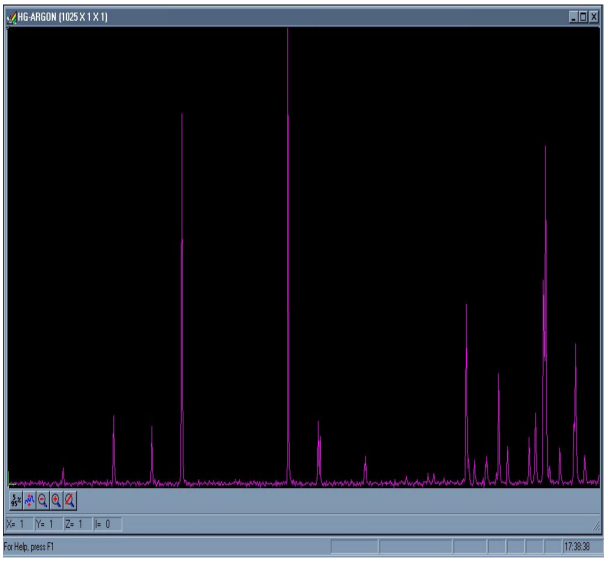

Fig. 4. Post-processed Hargon spectrum

5. SUMMARY AND CONCLUSIONS

We have presented, in the first approach, the implementation of Fourier Transform-Infrared spectrophotometer, especially in terms of pollutant signal processing. For analyzing interreflection effects most diagnosically, high reflectance filters should be available with both wide and restricted spectral ranges of transmission but in all cases with simple shapes of transmittance profile, preferably quasi-rectangular [11].

High reflectance filters with a very restricted trasmittance band (in practice an interference filter) are particulary good at revealing the different multiple modulated components and separating them from the non - multiply modulated ones which are also revealed.

Ideally, sets of these with a progressive sequence of trasmission band covering the whole spectral range of interest would be needed, a rather expensive proposition. It is an advantage for one side to be of high reflectance and the other side to be of low reflectance. Then one can turn the filter round to distinguish closely related categories of error [12].

In addition to these high reflectance diagnostic filters, low reflectance filters calibrated to an acceptable level of absolute uncertainty at a range of trasmittance levels are needed. These should be sufficiently thick to avoid fragility, instability of figure and avoid problems with channel fringes.

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