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S. Snyder

*Robinair Division*

K. Manz

*Robinair Division*

J. Willis

*Asoma Instruments*

R. Tobias

*Hitek Hardware*

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# PORTABLE REFRIGERANT IDENTIFICATION BY NEAR INFRARED SPECTROPHOTOMETRY

Sandra Snyder, Robinair Div. SP<sup>X</sup> Corp., Montpelier, OH;  
James Willis, Asoma Instruments, Inc., Austin, TX;  
Reginald Tobias, Hitek Hardware, Inc., Lancaster, MA;  
Kenneth Manz, Robinair Div. SP<sup>X</sup> Corp., Montpelier, OH

*Near infrared (NIR) spectrophotometric analysis has many advantages over physical property investigations for refrigerant type identification. Two facets where NIR analysis excels are the accuracy in detecting mixtures of refrigerants and the number of refrigerants capable of being identified. NIR provides a fingerprint of the substance analyzed which gives a much more accurate representation compared to a single physical property measurement. The sophisticated analysis of NIR can be transformed for field use so that air conditioning and refrigeration technicians can deal with the numerous types of refrigerant in the market today and that will emerge in the future. Patent applications have been filed on the NIR technology and subsequent use in portable refrigerant identification.*

## INTRODUCTION

### Analysis of need

Since section 608 of the Clean Air Act prohibits venting refrigerants it is now general practice to recover and recycle or reclaim the refrigerant. Also, as a result of the Montreal Protocol, new production of chlorofluorocarbon (CFC) refrigerants (R-11, R-12, R-500, R-502) will be phased out by 1996 and the phase out of hydrochlorofluorocarbon (HCFC) refrigerants (R-22) will occur at a later time. Interim and long term replacements for CFC refrigerants have been identified and are now being charged into retrofitted and new equipment. The process of selecting candidate replacements for HCFC refrigerants is not complete. Many of the replacement refrigerants are zeotropic blends which can selectively leak one or more of the constituents.

The combination of many more refrigerants in use during the phase out period and the widespread recycling of refrigerants is expected to increase the frequency of inadvertently mixing refrigerants. The industry is depending on the recycled supply of refrigerant to handle service requirements beyond the phase out. Since the inadvertent mixing of refrigerants has long been considered an irreversible process, it is important for service technicians to carefully maintain the supply of refrigerants. The penalty for using improperly mixed refrigerants is the possible loss in system performance and reliability.

Recycling equipment is capable of removing contaminants, such as moisture and acids from refrigerant. A field instrument is needed to determine the type of refrigerant and its level of purity with respect to other refrigerants in a storage container or refrigeration system. This analysis will improve service practices such as recovering, recycling, and reclaiming refrigerants in a manner to minimize inadvertent mixing and protect the purity of the refrigerant supply.

### Comparison to Other Methods

One of the most common methods for determining refrigerant type is to use the pressure/temperature saturation curves for each refrigerant. This works well for identifying several different types, but falls short when trying to distinguish between refrigerants and their replacements which are designed to have the same pressure/temperature curve. Other physical measurements using thermal conductivity, ultrasonics, dielectric strength, boiling point, and so forth may be able to distinguish between refrigerants and their replacements. However, physical measurements can easily be fooled by inadvertently mixed refrigerants. For example, 50 % of one refrigerant and 50 % of a second refrigerant may give the appearance, by virtue of a physical measurement, as being a third totally different refrigerant. The combination of several different physical measurements may help sort out this problem, but there is a limit to the accuracy that can be achieved by such methods.

The air-conditioning and refrigeration industry standard laboratory test is to use a gas chromatograph (GC) to analyze refrigerants for type and composition. In order to use gas chromatography, the service technician must take a liquid sample of the refrigerant, send the sample to a chemical laboratory, and wait several hours or days for the results. Meanwhile, an experienced laboratory technician must perform the analysis on an expensive GC. Also, the GC must be frequently calibrated. The gas chromatograph is used because it provides a "fingerprint" of the substance that was analyzed. A fingerprint provides a much more accurate representation of a substance compared to a single physical property. Near infrared spectrophotometry also analyzes chemicals by "fingerprinting" them.

## CONCLUSIONS

Use of near infrared technology in determining refrigerant type in the field will enable field technicians to have better control of their refrigerant supplies. Currently, fifteen common refrigerants can be identified qualitatively to within 2 % purity from other contaminant refrigerants. Future studies will include adding new refrigerants as they gain popularity and quantitative analysis of constituent refrigerants. With quantitative analysis the percentage of each refrigerant present in both inadvertent mixtures and manufactured refrigerant blends can be determined.

## APPARATUS AND TEST METHOD

### Test Cell Filling

Typical contaminants in refrigeration systems such as moisture, non-condensable gases, oil, and particulates, must be transparent to a refrigerant type analyzer. The near infrared regions of interest will not be affected by moisture or non-condensable gases. On the other hand, oil will cause problems with the optical windows. For this reason, vapor samples are drawn from the refrigerant supply to minimize the amount of oil that can enter the analyzer.

In order to obtain a liquid sample of refrigerant to analyze, the test cell is first evacuated to clear the cell of the previous sample. The cell is then cooled with a thermoelectric cooler to a temperature lower than the ambient temperature of the candidate refrigerant. Thus, the vapor refrigerant is introduced into the cell by virtue of both a temperature and pressure gradient. In preparation for the incident light beam, the refrigerant sample is condensed to liquid phase and maintained at a constant temperature by a proportionally controlled thermoelectric cooler.

### Optical Principles and Mechanism

In near infrared spectrophotometry (NIR) a light beam consisting of many wavelengths passes through a liquid sample. The liquid sample absorbs some of the wavelengths and transmits the others. A detector measures the amount of each wavelength that is transmitted. NIR fingerprints correspond to a pattern of transmissions at each wavelength. The refrigerant analyzer contains a training set of fingerprints for each refrigerant it can identify. A microprocessor algorithm computes a "distance" between an unknown refrigerant sample's fingerprint and each of the training set fingerprints. The smallest distance corresponds to the identity of the unknown.

The accuracy of an optical measurement depends on the long term stability of the optical components and electronics used in the spectrophotometer. We use two techniques in the NIR analyzer to assure long term stability and accuracy. The first technique, the use of a double beam, assures stability even though the lamp and detector may change their characteristics over time. The second technique, beam chopping, extends the precision and stability of the electronics by reducing the noise or short term fluctuations in the measurements. Figure 1 shows a plan view of the optical path used in the NIR analyzer.

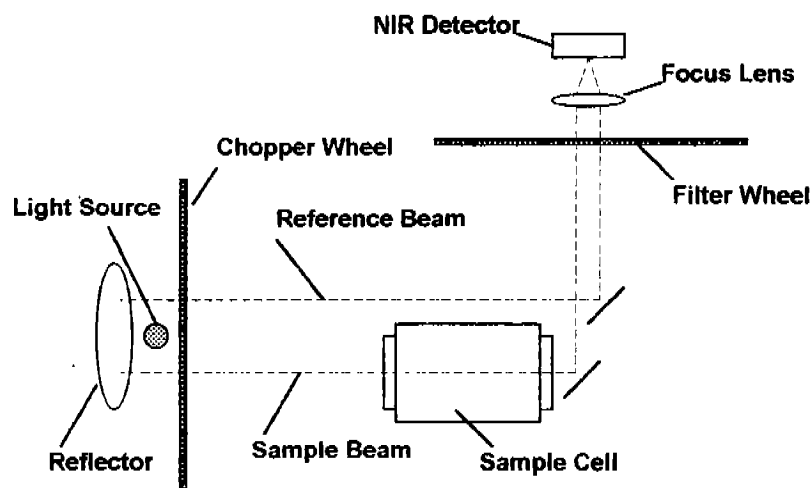


Figure 1 - Plan view of the optical path for the NIR analyzer.

### Double-Beam Spectrophotometers

In the NIR analyzer the light source is split into two beams. The sample beam passes through the sample cell; the reference beam goes directly to the detector. By taking the ratio of sample to reference beam, the double beam system compensates for source intensity drifts, changes in the source spectral distribution, wavelength efficiency variations, and detector sensitivity variations.

### Chopper Principles

The precision of a measurement is often limited by the electronic noise present in the circuitry. The most common noise source is called 1/f or flicker noise. Flicker noise is most intense at dc frequency and decreases with increasing frequency. By chopping the light beam, we are able to avoid making a dc measurement and can amplify and measure the detector's response at some higher frequency. The chopper also allows us to measure first the reference beam, then the sample beam and then "dark" or no beam.

In the NIR analyzer, the two beams are collimated using a parabolic reflector and pass through a motor driven chopper wheel. The holes in the chopper wheel are arranged to precisely transmit the reference, sample and dark beams.

Mirrors are used to fold the light path 90 degrees before passing through one of several infrared transmission filters. The filters were chosen based on a careful examination of the spectra obtained from a comprehensive set of refrigerants. Simulations of the characteristics of the available filters using a laboratory scanning spectrophotometer verified that this approach would yield the required performance. An eight position filter wheel is attached to a stepper motor to provide for filter selection. After the filter, an ordinary lens is used to focus the two beams onto an infrared detector. The detector is electrically and thermally isolated from the rest of the spectrophotometer in order to minimize noise.

## THEORY OF OPERATION

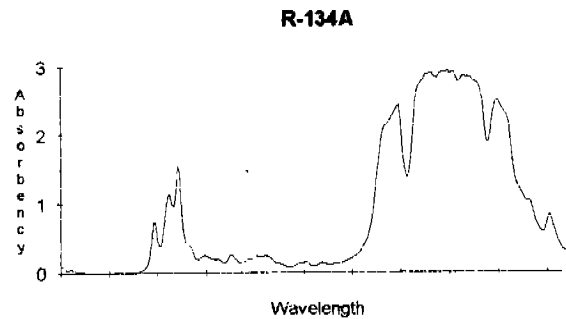
### Absorption Spectrophotometry

Near Infrared (NIR) absorption methods measure the amount of the light that is absorbed by the sample. In ideal situations, (one component in an otherwise non-absorbing matrix), the absorption of light follows Beer's law;

$$A = -\log(T) = a \cdot b \cdot c \quad (1)$$

where  $A$  is the absorbancy,  $T$  is the transmittance,  $a$  is the absorptivity,  $b$  is the path length of absorption, and  $c$  is the concentration of the absorbing species. If  $b$  is expressed in cm,  $a$  has the units of  $(\text{conc})^{-1} \text{cm}^{-1}$ . Quantitative analysis methods involve measuring the amount of light that is absorbed by the sample, calculating the absorbancy, and relating the absorbance to concentration.

A typical absorption spectrum has a series of absorption bands. These bands are actually overtones of the primary absorption bands which occur in the infrared (IR) spectrum rather than the NIR. The position, width and height of the absorption bands depends on the composition of the sample and is a signature for that particular sample. Qualitative analysis is performed by acquiring a spectrum of the unknown sample and comparing it to a series of previously acquired "training" standards. A typical refrigerant spectrum is shown in Figure 2.



**Figure 2 - NIR spectrum or "fingerprint" of R-134a. The absorption occurs in three narrow bands on the left hand side of the spectrum as well as several broad bands on the right hand side. This complex spectrum of a typical NIR experiment indicates the need for a high quality design and careful component selection in the NIR spectrophotometer.**

### **Selection of Particular Wavelengths for Refrigerant Analysis**

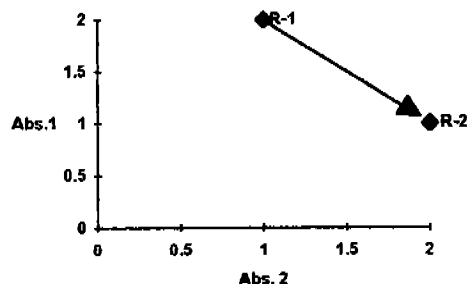
Careful study of spectra taken from a comprehensive set of refrigerants revealed the spectra can be distinguished from each other by concentrating on a series of absorption bands. Qualitative analysis is performed by measuring the absorption in a series of bands for the set of training standards, then comparing these with the absorption from the unknown sample. Currently we are measuring absorbancy in five bands, which are sufficient to analyze the target matrix of refrigerants and contaminants.

### **Distance Measures**

The comparison of the unknown sample to the training set involves some form of "distance" measure. In other words, "How close is this unknown sample to each of the training samples?" We then pick the "closest match" from the set of training samples. If the match is close enough, we assume the unknown is the same as one of the training samples and report the result. If the match is not very close, we report "No Match". In order to distinguish both pure and contaminated samples, the training set must contain each of the pure samples and a large number of contaminated samples.

### **A Two Dimensional Example**

To understand how we measure the distance between two NIR measurements, consider the following simple example. Assume we have measured the absorption in two bands for two different samples. The absorbancy for refrigerant R-1 in band one is 2 and in band two is 1. The absorbancy for refrigerant R-2 is just the reverse, absorbancy of 1 in band one and 2 in band two. This example is plotted in Figure 3.



**Figure 3 - The absorbancy in two absorption bands for two different hypothetical refrigerant samples. Here R-1 has absorbancy of (1,2) and R-2 has absorbancy of (2,1). The RMS distance, shown by the arrow, between R-1 and R-2 is the square root of two or 1.414.**

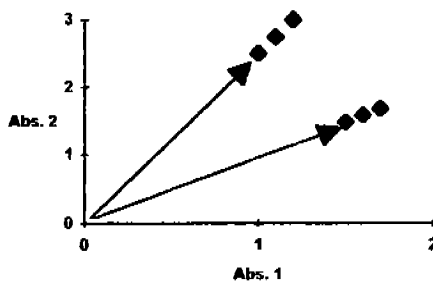
One familiar technique for measuring distance is the root mean square (RMS) of the differences of the absorbancy in the two bands. In this example the RMS difference is:

$$\sqrt{(2-1)^2 + (1-2)^2} = \sqrt{2} \quad (2)$$

A number close to zero indicates a close match and a large number indicates a poor match. This technique can be extended to any number of absorption bands simply by adding more terms.

In NIR absorption spectrophotometry, similar samples or replicate measurements on the same sample tend to cluster along lines which radiate from the origin. A hypothetical example of this is shown in Figure 4. Another way to measure the "best match" is to measure the angle between the two measurements and the origin. If the samples are similar, then the angle is zero. If they are very different, then the angle can be as high as 90 degrees.

In the examples given here, we have shown only two absorption bands, however, several bands are used in a typical NIR spectrophotometer. Just as with the RMS technique, the angle concept can be extended to any number of absorption bands.



**Figure 4 - Absorbancy of several replicate samples of refrigerants. The different absorption measurements tend to fall in clusters which are directed toward the origin. The arrows indicate the angle between two measurements.**

## PRESENTATION AND ANALYSIS OF RESULTS

For example, we analyzed a set of nine refrigerants using a scanning spectrophotometer with settings which approximated the performance of a filter based spectrophotometer. We then converted the absorbance spectra to transmission and integrated the transmission over the bandwidth of the filters

we had selected. This represents the raw signal from each transmission filter. We then normalized each one to the transmission of filter number one and then converted the transmission values back to absorbancy. Filter one was chosen because it had no significant absorption with any of the refrigerants we tested. Finally we compared the absorbancy from each sample to each of the other samples using the "square root of the sum of the squares" technique. The results are shown in the following tables:

**Table 1: Calculated RMS distances for the primary seven refrigerants. This data was obtained by measuring the absorbancy on a scanning NIR spectrophotometer and calculating the absorbancy using the bandpass characteristics of selected transmission filters. The numbers shown are the RMS distances of the normalized absorbancies of the training samples. Here a perfect match is indicated by a zero value, while large numbers indicate a significant deviation from the training sample.**

	HP62	R402B	R12	R134a	R22	R401A	R502
HP62	0.0000						
R402B	0.9902	0.0000					
R12	2.8828	1.9551	0.0000				
R134a	0.6117	0.8108	2.4696	0.0000			
R22	1.6177	0.6583	1.4121	1.3724	0.0000		
R401A	1.0049	0.2069	1.9943	0.8871	0.6274	0.0000	
R502	1.9799	1.0214	0.9792	1.6565	0.4343	1.0301	0.0000

**Table 2: The RMS distance for R-11 and R-123. The values shown were obtained in the same manner as those in Table 2.**

	R11	R123
R11	0.0000	
R123	1.3730	0.0000

### Analysis of Results

The NIR analyzer is capable of measuring changes in absorbencies down to about 1 part in 4000. The ratio of the distance values to the magnitude of absorbance is an indication of the relative change in the readings when one refrigerant is compared to another. The smallest distance shown in Table 1 is about 0.2. Typical absorbencies range from 2 to 3, so this represents a change of 6 to 10% relative. If we multiply the distance value obtained with the pure sample by its concentration we have an estimate of the reading we would obtain with a diluted or contaminated sample. For the worst case of a mixture of R-402B and R-401A, a contamination ratio of 1 part in 240 gives a change in the reading of 1 part in 4000 ( $0.06 \times 4000=240$ ). This implies the NIR analyzer is capable of measuring contamination to better than 0.5%. However, other sources of error, such as temperature effects, calibration errors and sampling errors may increase this value by factor of two.

## **SIGNIFICANCE AND POSSIBLE FUTURE DEVELOPMENTS/IMPROVEMENTS**

Currently the NIR analyzer uses strictly qualitative methods to determine the type of refrigerant and whether the refrigerant is pure enough for reuse or requires incineration. In the future if more information about the exact composition of the refrigerant is needed, we will explore interpolation methods which permit quantitative analysis. If the exact composition of a mixture is known, then it can be diluted or remixed to provide a usable refrigerant. For example, should azeotropic refrigerant blends selectively leak one component over time, we would have the ability to measure the composition and bring the blend back to within new refrigerant specifications.