

Ultrasonic Measurement of Molar Fractions in Gas Mixtures by Orthogonal Signal Correction

J. E. Carlson*, P.-E. Martinsson

EISLAB, Dept. of Computer Science and Electrical Engineering, Luleå University of Technology, SE-971 87 Luleå, Sweden.

*Email: Johan.Carlson@csee.ltu.se

Abstract— Within Sweden and the EU, an increased use of biogas and natural gas is encouraged. To support more effective manufacturing, distribution, and consumption of energy gases, new methods for the measurement of the calorimetric value or the gas composition are needed.

In this paper we present a method to quantify variation in ultrasound pulse shape, caused by interaction effects between the constituents of a two-component gas mixture.

The method is based on a combination of *Principal Component Analysis* [1] and *Orthogonal Signal Correction* [2]

Experiments on mixtures of oxygen and ethane show that the extracted information correlates well with the molar fraction of ethane in the mixture.

I. INTRODUCTION

Natural gas contains a mixture of several gases, like methane, ethane, hydrogen, etc. Sometimes also small, but highly undesired fractions of oxygen. With the use of different sources of gas (i.e. different gas fields) the energy content of the gas delivered to customers may vary considerably. Variations up to 20% are common [3]. It is of interest to both provider and customer to know the composition of such gas mixtures, since this determines the energy content (calorimetric value) and thus, the combustion properties and the monetary value of the gas.

Today, the energy content of gases is measured using either gas chromatography or calorimetry. Both methods are accurate, but require samples of the gas to be removed and analyzed separately, which makes them relatively slow. They are also relatively expensive. Because of this, the existing techniques are not suitable for on-line measurement at the customer side of the distribution line.

Typically, both the speed of sound and the attenuation of sound within a gas vary with temperature, frequency, pressure, etc. Hence, both these parameters can help to monitor changes in experimental conditions. This has recently been studied in both theory and experiments by Dain and Lueptow [4], [5], Martinsson [6], and Townsend and Meador [7].

The frequency dependence of the attenuation is fairly easy to measure, but the speed of sound is much more difficult [8]. Both of these affect the shape of the received pulse. In this paper we develop a method to empirically quantify changes in pulse shape, and evaluate this for mixtures of oxygen and ethane.

Fig. 1 shows three pulses obtained using the experimental setup described in Sec. III-A. The first pulse was measured in pure oxygen, the second in pure ethane, and the third in a mixture of the two, containing molar fraction of 40% of

ethane. As the figure shows, there is a small change in pulse shape between pure oxygen and ethane. It is, however, more difficult to notice how this changes when mixing the gases.

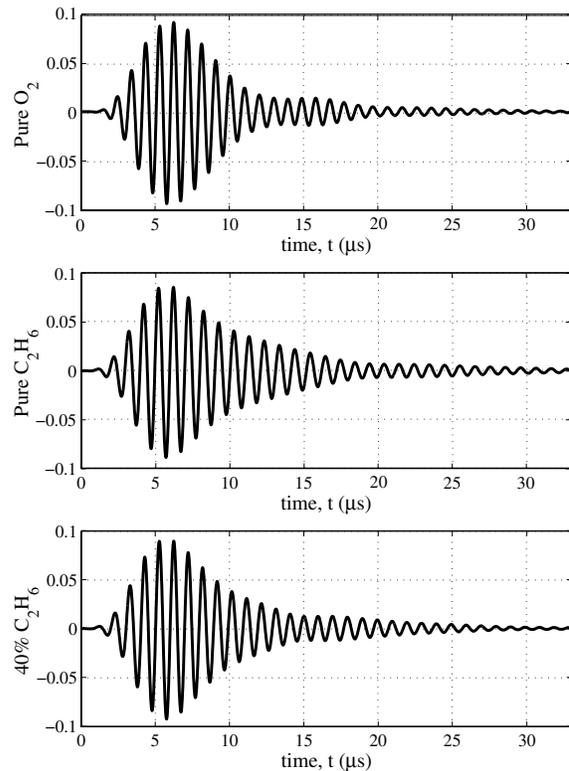


Fig. 1. Example of pulses measured in pure oxygen, pure ethane, and a mixture with a molar fraction of 40% ethane, all measured at a static pressure of 5.0 bar. The temperature was 20 °C.

In this paper, we develop a subspace-based filter, that can be used to suppress variations in pulse shape originating from the pure gases. The filter is based on a principle known as *Orthogonal Signal Correction* (OSC) [2]. Pulses measured in a mixture will be affected by the pure gases, and by the inter-gas interaction effects. These interaction effects are much smaller than the effects of the pure gases, but highly interesting when the goal is to study the composition a mixture. The OSC filter is implemented as a projection matrix that projects the measured pulses onto the orthogonal complement of a basis spanning the experimental variation caused by the pure gases. The remaining experimental variation is then analyzed using PCA [1].

The technique is evaluated with experiments on pure oxygen (O₂), pure ethane (C₂H₆), and mixtures of the two, for molar fractions of ethane in the range of 20%–80%. The results show that the remaining variation can be explained by one principal component, which correlates well with the molar fraction of ethane.

II. THEORY

Principal Component Analysis (PCA) [1] is a powerful tool for analyzing multivariate data. The central idea is to reduce the dimensionality of a data set consisting of a large number of interrelated variables, but at the same time preserving as much as possible of the systematic experimental variation in the data.

In the experiments (see Sec. III-B), we have two data sets. The first containing pulse-echo measurements of pure oxygen and pure ethane, and the second containing measurements on mixtures of the two. If the effects of oxygen and ethane were to add linearly when mixing the two, the dimensionality of the data set would not increase. That is, the same principal components could be used to describe the experimental variation in both data sets. If, however, there are any interaction effects between the gases in the mixture, we would need some additional principal components to describe these (i.e. the dimensionality of the data set is increased). Now, if the interaction effects are small, which they will certainly be when the molar fraction of one of the gases is small, they will be practically drowned by the effects of the pure gases.

If the goal is to quantify the effect of mixing gases we need some method to remove the effects originating from the pure gases. The way we approach this problem is by *Orthogonal Signal Correction* (OSC) [2]. This process can be seen as a filter, suppressing the effects of the pure gases by projecting the whole data set onto a subspace *orthogonal* to the subspace spanned by the pure gases. In order to do this, we first need to find a basis for the variation caused by the pure gases. This is obtained by performing a PCA on the first data set (containing only measurements of pure gases). For this to work, the data set has to be pre-processed to remove the effect of propagation delay and scalar attenuation. This information is, of course, still accessible, but by removing these effects, we do not *a priori* assess any greater significance to any of the measured pulses, even if they are more attenuated. The aim here is to study changes in pulse shape.

The next subsection will describe the pre-processing of the ultrasound pulses, and Sec. II-B then describes the OSC and the PCA.

A. Pre-Processing

The pre-processing consists of two steps:

- 1) Normalizing the pulses to unit energy, thus removing the effect of a scalar attenuation due to the propagation distance.
- 2) Aligning the pulses in time and thereby removing the effect of changes in propagation delay through the medium, and the effect of any sampling jitter caused by the digitizing hardware.

The time-delay estimation is done by combining a standard cross-correlation estimator (to obtain an estimate in whole samples), and then refining the estimate using the sub-sample estimator by Grennberg and Sandell [9].

B. Orthogonal Signal Correction

After the pre-processing, we are left with a set of measurements that essentially vary only in pulse shape. In this section, we describe the remaining steps of the analysis, that is:

- 1) Find a basis for the experimental variation caused by the pure gases (PCA), for oxygen and ethane, for different static pressures.
- 2) Project the measurements of mixtures onto the orthogonal complement of the basis determined in step 1 (OSC).
- 3) Find a new basis for the remaining experimental variation (PCA).

Let \mathbf{X}_0 be a matrix where the columns are pulses measured in pure oxygen (O₂) and pure ethane (C₂H₆), for different pressures. Let \mathbf{X}_1 be the matrix with columns corresponding to mixtures of the gases, each representing different molar fractions of ethane.

Finding a basis of for the experimental variation spanned by the columns of \mathbf{X}_0 means determining the principal components (PC:s) of \mathbf{X}_0 . In this paper, the PCA is implemented using *Singular Value Decomposition* (SVD) [10]. With the SVD, any rank r matrix \mathbf{X}_0 can be factored as:

$$\mathbf{X}_0 = \mathbf{U}_0 \mathbf{S}_0 \mathbf{V}_0^T, \quad (1)$$

where the columns of \mathbf{U}_0 and \mathbf{V}_0 are the unit-norm eigenvectors of $\mathbf{X}_0 \mathbf{X}_0^T$ and $\mathbf{X}_0^T \mathbf{X}_0$, respectively. The non-zero diagonal elements, σ_i of \mathbf{S}_0 are the square-roots of the eigenvalues of $\mathbf{X}_0 \mathbf{X}_0^T$ and $\mathbf{X}_0^T \mathbf{X}_0$, sorted so that $\sigma_1 \geq \sigma_2 \geq \dots \geq \sigma_r$. This can be seen as a change of basis, where the new basis for the columns of \mathbf{X}_0 is given by the columns of \mathbf{U}_0 (also called *principal components* or *loading vectors*), and the weights for the new basis (*scores*) are given by the columns of $\mathbf{S}_0 \mathbf{V}_0^T$.

The change of basis means that all pulses (columns of \mathbf{X}_0) can now be represented as a linear combination of the columns in \mathbf{U}_0 , using the weights in $\mathbf{S}_0 \mathbf{V}_0^T$.

To examine how much of the total experimental variation (in %) each column in \mathbf{U}_0 explains, we study the scaled singular values. Let $\bar{\sigma}_i$ be scaled versions of the r non-zero singular values σ_i , as

$$\bar{\sigma}_i^2 = 100 \frac{\sigma_i^2}{\sum_{k=1}^r \sigma_k^2}. \quad (2)$$

Now, if the effects of the constituent gases would add linearly, then the same set of basis vectors (columns of \mathbf{U}_0) would also span the variations in pulse shape caused by the gas mixtures. That is, the columns of \mathbf{X}_1 could all be written as linear combinations of the columns of \mathbf{U}_0 . If this is not the case, a basis for the additional variation, i.e. inter-gas interaction effects, will be given by $\tilde{\mathbf{U}}_1$, where

$$\tilde{\mathbf{X}}_1 = \tilde{\mathbf{U}}_1 \tilde{\mathbf{S}}_1 \tilde{\mathbf{V}}_1^T, \quad (3)$$

where

$$\tilde{\mathbf{X}}_1 = \mathbf{\Pi}_{\mathbf{X}_0}^\perp \mathbf{X}_1, \quad (4)$$

i.e. the SVD of the matrix \mathbf{X}_1 , after projecting onto the orthogonal complement of \mathbf{X}_0 . The projection matrix $\Pi_{\mathbf{X}_0}^\perp$ is given by [10]:

$$\Pi_{\mathbf{X}_0}^\perp = \mathbf{I} - \hat{\mathbf{U}}_0 \left(\hat{\mathbf{U}}_0^T \hat{\mathbf{U}}_0 \right)^{-1} \hat{\mathbf{U}}_0^T, \quad (5)$$

where $\hat{\mathbf{U}}_0$ is the matrix consisting of the n ($n < r$) most significant components of \mathbf{U}_0 . This is determined by looking at the cumulative sum of the scaled singular values from Eq. (2).

Since the columns of $\hat{\mathbf{U}}_0$ are by construction orthonormal [10], Eq. (5) simplifies to

$$\Pi_{\mathbf{X}_0}^\perp = \mathbf{I} - \hat{\mathbf{U}}_0 \hat{\mathbf{U}}_0^T, \quad (6)$$

In other words, we can say that the columns of $\tilde{\mathbf{U}}_1$ form a basis for the experimental variation that remains after removing the contribution of the pure gases. The matrix $\Pi_{\mathbf{X}_0}^\perp$ in Eq. (6) projects the data in \mathbf{X}_1 onto a smaller subspace, orthogonal to the subspace spanned by $\hat{\mathbf{U}}_0$. This is why this process is called *Orthogonal Signal Correction*.

C. Summary of the Algorithm

The analysis principle described in the previous sections can be summarized as:

- 1) Normalize and align the pulses as described in Sec. II-A.
- 2) Calculate principal components (\mathbf{U}_0) of the pure gases using Eq. (1).
- 3) Remove the effect of the pure gases from the gas mixture, using Eq. (4).
- 4) Determine the principal components, $\tilde{\mathbf{U}}_1$, of the remaining variation ($\tilde{\mathbf{X}}_1$), using Eq. (3).

III. EXPERIMENTS

A. Experimental Setup

A pulse echo measurement scheme was used to measure the attenuation and speed of sound for oxygen and ethane. The acoustic properties of interest vary with frequency, f , and pressure, P . The temperature and frequency dependence on sound velocity and acoustic attenuation, has previously been investigated by, for example, Martinsson [6], Lueptow [4], [5], and Bhatia [11]. Changes in frequency and pressure are normally studied as the ratio f/P [4]. In this paper, a 1 MHz air transducer was used while the static pressure was varied.

A custom-built pressure chamber (see Fig. 2) was used to achieve different static pressures. The pressure was varied between 1.54 to 7.4 bar in 12 steps for each gas. Since the attenuation in ethane is extremely high at low pressures and high frequencies, we were limited to make measurements at higher pressure for that particular gas (above 1.86 bar).

The pressure in the chamber was measured with an *ANDERSON TPP Pressure Transmitter*. The transmitter has an accuracy of approximately 30 mbar. This includes the combined effects of linearity, hysteresis and repeatability.

The transducer was mounted on a stainless steel measurement cell, as seen in the lower left corner of Fig. 2. The measurement cell was then immersed into the pressure chamber. The whole setup was then placed in a temperature controlled

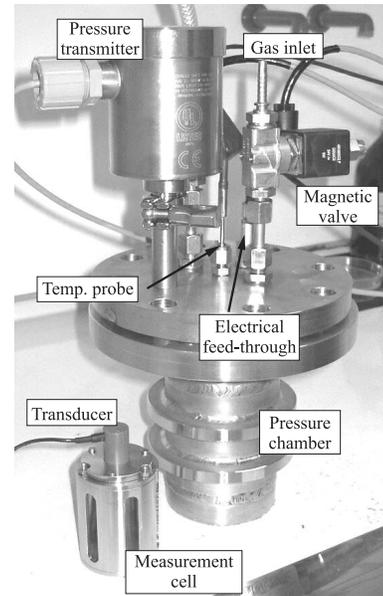


Fig. 2. The measurement equipment. All measurements were performed in a pressure chamber. The pressure was varied between 1.54 bar and 7.4 bar. The air transducer has a center frequency of 1 MHz.

chamber (*Heraeus Vötsch HT4010*), where the temperature could be kept at a constant.

To excite and receive acoustic pulses from the transducer, a *Panametrics Pulser/Receiver Model 5072* was used.

All pulses were sampled with a *Tektronix TDS 724*, 1 GHz oscilloscope. For each experimental setting, 50 pulses were recorded and transferred to a PC for further processing.

For each measurement, the temperature was recorded using an encapsulated PT100 sensor mounted through the wall of the pressure chamber.

B. Experiments

The first set of experiments was with pure ethane and pure oxygen, at 20 °C, for pressures of 1.54–7.4 bar. This resulted in 12 measurements of ethane and 12 of oxygen. After aligning and normalizing, as described in Sec. II-A, all 24 were stored as columns of the matrix \mathbf{X}_0 . The second set of experiments was with mixtures of ethane and oxygen, for molar fractions of 20%, 40%, 60%, and 80%, for the same pressure range, also at 20 °C. These pulses were then stored as columns of the matrix \mathbf{X}_1 .

C. Results

Following the steps of described in Sec. II-C, we first obtain a basis for the experimental variation in the pure gases. The basis vectors (Principal Components) are the columns of \mathbf{U}_0

Looking at the cumulative sum of the scaled eigenvalues (Eq. (2)), $\bar{\sigma}_i^2$, we saw that the first three components are enough to describe approximately 99% of the total experimental variation (c.f. Fig. 3). The matrix $\tilde{\mathbf{U}}_0$ is thus given by the first three columns of \mathbf{U}_0 .

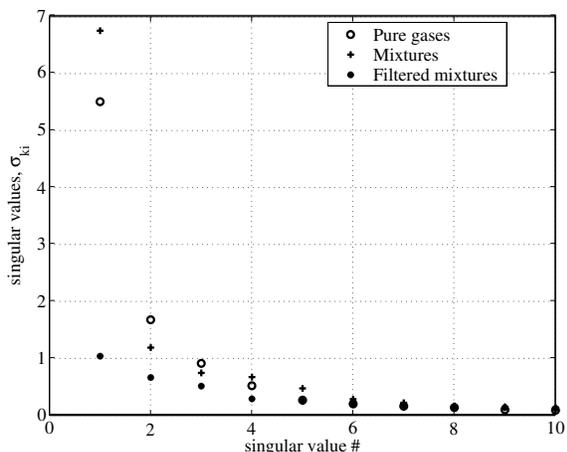


Fig. 3. Singular values of the pure gases (\mathbf{X}_0), the mixtures \mathbf{X}_1 and the mixtures after projection $\tilde{\mathbf{X}}_1$. It is clear that the pure gases contributes to most of the variation. The filtering reveals the relatively small interaction effects.

The OSC processing removes all experimental variation already explained by the linear effects of the pure gases. The remaining variation is significantly smaller and lies close to the noise level (c.f. Fig. 3). The interaction effects can essentially be described using only one of the principal components of $\tilde{\mathbf{X}}_1$.

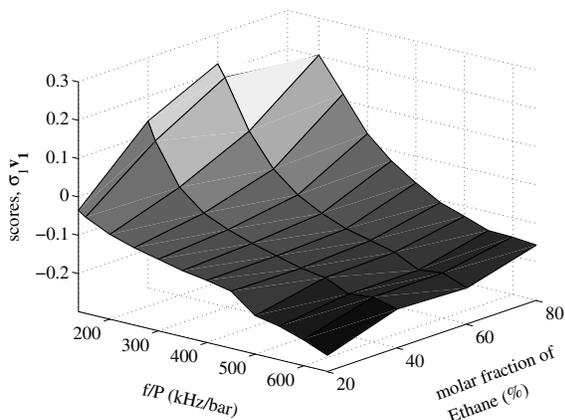


Fig. 4. Scores of the first principal component, $\tilde{\sigma}_1 \tilde{\mathbf{v}}_1$, of $\tilde{\mathbf{X}}_1$, as function of frequency to pressure ratio and molar fraction of ethane.

Fig. 4 shows the *scores* of the first component, as function of frequency to pressure ratio (f/P) and molar fraction of ethane. For high f/P values, the acoustic attenuation is very high, and the signal-to-noise-ratio (SNR) drops. For these f/P values, the inter-gas interaction effects are almost drowned by the experimental noise, and thus become difficult to extract. This can be seen in Fig. 4 as the surface reaches an almost constant level. For higher SNR, there is a strong correlation between molar fraction of ethane and the scores of the first principal component. This suggests that the inter-gas interaction effects can be quantified with this technique.

IV. DISCUSSION

The results presented in this paper show that it is possible to quantify effects on the shape of an ultrasound pulse, stemming from interaction effects between the constituent gases in a mixture. A question that we have not considered in this paper is *what underlying physical properties cause these interaction effects?*. Current research focuses on studying these phenomena, but to date, it is not possible to draw any conclusions regarding this.

In Fig. 4 there is a ridge for high pressures and approximately 50% of ethane. At first this might seem odd, but looking more closely at the algorithm it makes perfect sense. The OSC procedure removes variations in pulse shape, already described by the pure gases. When one of the gases are dominant in the mixture, the interaction effects should also be much smaller. The corresponding scores in Fig. 4 should therefore be almost zero under these conditions. For high pressures (low f/P values), i.e. when the SNR is high, the OSC process also succeeds in removing most of the variation. For low SNR values, this is not the case, which also shows in the lower right corner of Fig. 4.

In this paper we have only considered a two-component gas mixture. The long-term goal is to develop method for on-line measurement of the energy content of energy gases. In practice, these are always mixtures of more than two gases. Although molar fractions would enable us to calculate the energy content, it might be easier to quantify the energy content directly, using the same methodology as described in this paper.

In Sec. II-A, we mention the importance of aligning the pulses in time before processing. If this is not done, the time-delays will cause the dimensionality to increase (i.e. more principal components are needed). Compensating for the time-delays is more difficult than one might think. The change in pulse shape that we are interested in quantifying, is also a source of error when we try to estimate the time-delays. The reason for this is that the time-delay between pulses with different shape is not well-defined. Future research will have to incorporate a more accurate alignment algorithm.

V. CONCLUSIONS

In this paper we presented a technique for quantifying inter-gas interaction effects in a two-component gas mixture. The principles of *Principal Component Analysis* and *Orthogonal Signal Correction* were used to extract variations in the ultrasound pulse shape, not explained by looking at the constituent gases by themselves.

The experimental results show that, for a mixture of oxygen an ethane, the interaction effects can be described with only one principal component, and that the weights (coefficients) of this component correlate well with the molar fraction of ethane in the mixture.

VI. ACKNOWLEDGMENTS

The authors wish to express their sincerest gratitude toward Prof. Jerker Delsing, for supporting this work. Generous grants from the *Swedish Energy Agency* are also gratefully acknowledged.

REFERENCES

- [1] I. T. Jolliffe, *Principal Component Analysis*. New York: Springer Verlag, 2nd ed., 2002.
- [2] S. Wold, H. Antti, F. Lindgren, and J. Öman, "Orthogonal Signal Correction of Near-Infrared Spectra," *Chemometrics and Intelligent Laboratory Systems*, vol. 444, pp. 175–185, 1998.
- [3] J. Delsing and I. Blom, "On-Line Measurements of Energy Content of Bio Gas and Natural Gas Mixtures," Tech. Rep. ISSN: 0282-3772, Lund Institute of Technology, 1995.
- [4] Y. Dain and R. M. Lueptow, "Acoustic Attenuation in Three-Component Gas Mixtures - Theory," *J. Acoust. Soc. Am.*, vol. 109, pp. 1955–1964, 2001.
- [5] Y. Dain and R. M. Lueptow, "Acoustic Attenuation in Three-Component Gas Mixtures - Results," *J. Acoust. Soc. Am.*, vol. 109, pp. 1974–1979, 2001.
- [6] P.-E. Martinsson and J. Delsing, "Ultrasonic Measurements of Molecular Relaxation in Ethane and Carbon Monoxide," in *Proc. IEEE Int. Ultrason. Symp.*, (Munich, Germany), pp. 494–499, IEEE, October 8–11 2002.
- [7] L. W. Townsend and W. E. Meador, "Vibrational Relaxation and Sound Absorption and Dispersion in Binary Mixtures of Gases," *J. Acoust. Soc. Am.*, vol. 99, pp. 920–925, 1995.
- [8] J. E. Carlson, F. Sjöberg, and P.-E. Martinsson, "A Noise-Tolerant Group Delay Estimator Applied to Dispersion Measurement in Gases," in *Proc. IEEE Int. Ultrason. Symp.*, (Honolulu, Hawaii, USA), pp. 254–257, IEEE, Oct. 5–8 2003.
- [9] A. Grennberg and M. Sandell, "Estimation of Subsample Time Delay Differences in Narrowband Ultrasonic Echoes Using the Hilbert Transform Correlation," *IEEE Trans. Ultrason., Ferroelec., and Freq. Contr.*, vol. 41, no. 5, pp. 588–595, 1994.
- [10] G. Strang, *Linear Algebra and its Applications*. San Diego: Harcourt Brace Jovanovich, 3rd ed., 1986.
- [11] A. B. Bhatia, *Ultrasonic Absorption - An Introduction to the Theory of Sound Absorption and Dispersion in Gases, Liquids and Solids*. New York: Dover Publications, 1985.