
Analysis of Engine Oil and Phosphorus Volatility

T.W. Selby
Savant, Inc., Midland, MI, USA

Abstract

An apparatus has been designed that allows the measurement of phosphorus volatility, which is important in, among other things, controlling the degradation of exhaust catalysers in automobiles. Following on from the original Noack volatility test, the Selby–Noack apparatus can measure up to 99.9% of volatiles. The apparatus has been used in the present work to assess the relationship between engine oil volatility and engine oil phosphorus volatility (from additives), some reflections on which are presented.

Keywords

engine oil, phosphorus, volatility, Noack, emissions

INTRODUCTION: Early concerns with volatility

The volatility of engine oil has been a concern to engine manufacturers since two- and four-cycle engines were first commercialised in the early 1900s. Early motorists were often required to carry spare containers of oil to replace that which was lost either through leakage or, most usually, through passage into the combustion chamber and being burned or volatilised.

Leakage past the piston rings and down the valve guides was more of a problem than simple loss of lubricating oil. If the oil had a tendency not only to leak but also readily to form deposits, the engine owner was liable for a severe penalty in the form of a cycle of leakage, deposits, stuck rings, cylinder-wall scoring, and more leakage, spiralling down into a destroyed engine. Since some of the base oils used during the period up to the 1930s and 1940s were relatively high in naphthenic composition – and commensurately low in viscosity index (VI) – their viscosities fell more rapidly with increasing temperature. Thus, they not only leaked more readily past the piston rings and valve guides but, once there, were much more likely to form piston and combustion chamber deposits.

In contrast, paraffinic base oils with higher VIs leaked less readily into areas where they might burn or volatilise. For this reason, as well as because of easier startability, they became premium base stocks. Ultimately, in the late

1940s and early 1950s, other ways of accomplishing good viscosity control became available through the development of VI improvers and, with other additive advances, the age of designed lubricants came into being.

Modern concerns with volatility

The design of modern engines has resulted in drastically reduced oil consumption. However, by this very fact, the engine oil had to be much more sturdy in its service since the partial restitution of its additive by replacement of volatilised oil (top-up) has been therefore considerably reduced. This, in turn, has led progressively to the development of additives which, individually or collectively, serve as oxidation inhibitors, anti-wear agents, detergents, dispersants and VI improvers. Some of the more important of these additives were based on zinc-phosphorus chemistry and were very effective both as anti-oxidants and, more importantly, as anti-wear agents.

Emission effects With more recent efforts to control emissions from the automotive engine, oil volatility not only was seen as affecting engine deposits, but was also linked with emission catalyst poisoning because of the phosphorus content of the volatile product.¹

Noack test application As regards oil volatility, Noack's apparatus and test of the early 1930s² was further developed into a CEC volatility test in the early 1980s.³ To those who became additionally concerned about phosphorus volatility, it seemed appropriate to relate engine oil volatility and phosphorus volatility in an effort to control the latter problem area as well.

Further developments

The information and engine simulation character given by Noack's test was easily appreciated. The approach seemed superior to other methods, such as gas chromatography (which, while informative, tended to reflect a volatility associated with the separation dynamics of the packed columns and capillaries associated with the latter method). However, to avoid the associated use of Woods metal because of its toxic components and, in addition, to collect the volatiles for subsequent analysis, the author and his associates initiated work in 1993 to develop a considerably modified approach to Noack's test.

It was thought that such an approach could shed light on the relationship between oil volatility and phosphorus volatility. Three papers have been published⁴⁻⁶ on aspects of the work. This fourth paper gathers the critical information of the previous work, particularly in regard to phosphorus volatility,

Figure 1(a) Selby-Noack volatility testing apparatus

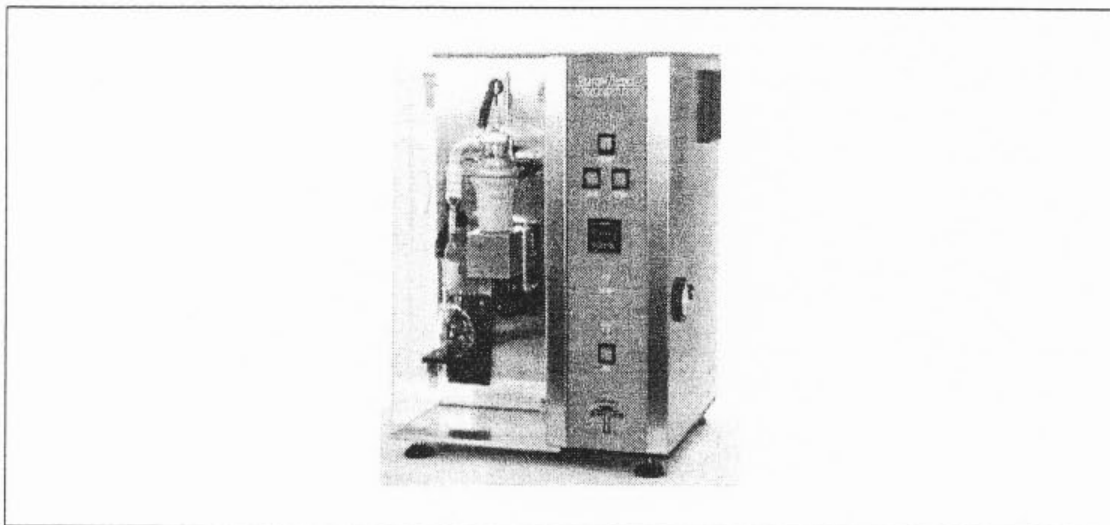
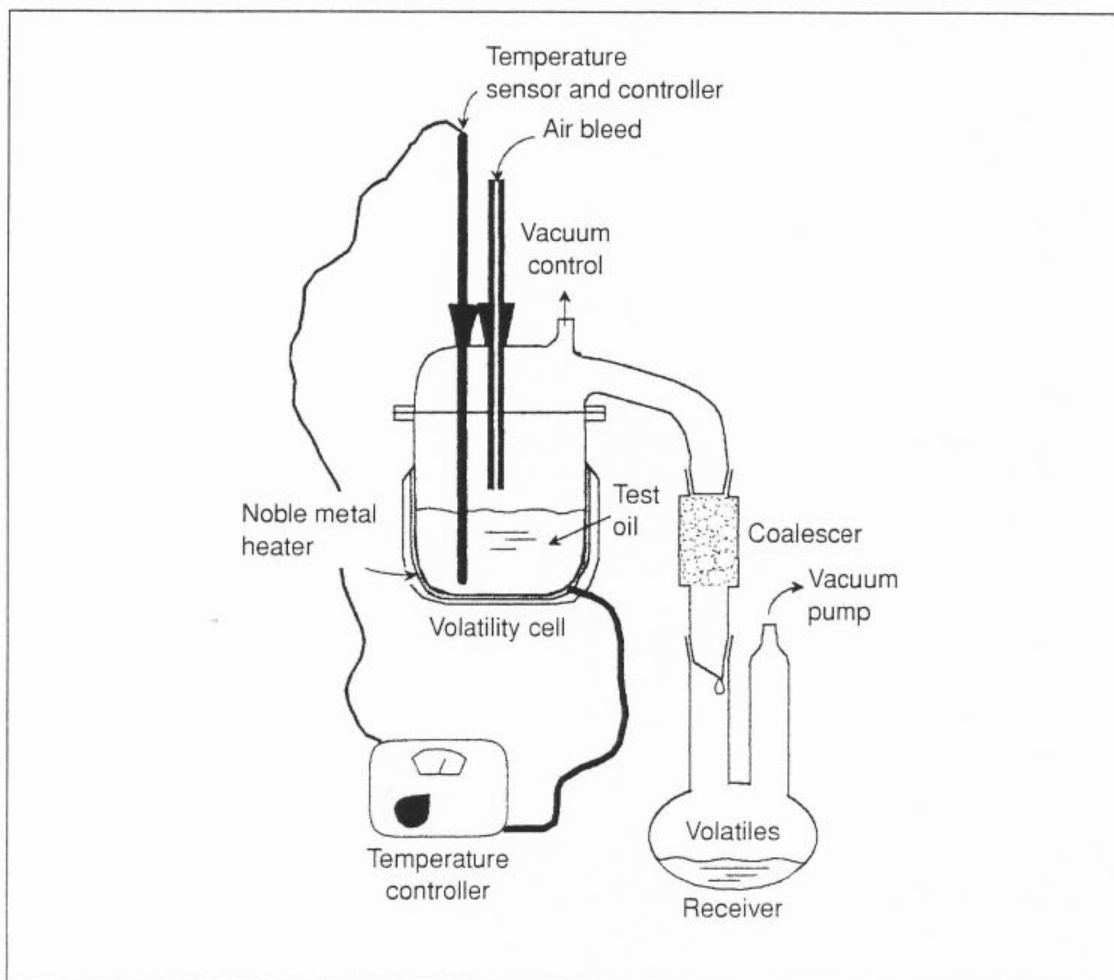


Figure 1(b) Selby-Noack volatility testing apparatus indicating critical elements



and presents new precision information obtained by using automatic vacuum control.

APPARATUS AND OPERATION

The Selby–Noack apparatus is pictured in **Figure 1(a)** and the essential components are given in **Figure 1(b)**. There are three critical elements.

The first is the volatilising cell (volatiliser) which is a specially designed glass vessel heated by a thin film of noble metal fused to the outer surface of the glass. The resistivity of this thin film provides the heat necessary to raise the temperature of the oil from room temperature to 250°C within six minutes. The temperature is held reasonably precisely to within $\pm 1^\circ\text{C}$ during the test by an on-board controller monitoring a temperature probe extending down into the test fluid.

The second element is a specially designed coalescer which both regulates the rate of air flow into the volatiliser and establishes the level of vacuum required. It also coalesces the volatilised oil very efficiently (see below).

The third element is the automatic vacuum control. This is a built-in electronic device which is sensitive to, and can modulate, vacuum to within a millimetre absolute pressure of water or less.

All three of these elements are desirable for best response of the apparatus, although the automatic vacuum control can be done by careful, but tedious, manual control during the duration of the hour test.

Test protocol

Set-up 65 g sample oil are weighed in the volatiliser to the nearest 0.01 g. The volatiliser is then coupled with its cap, the coalescer, and the receiver, and set into place behind the clear plastic door on the apparatus cabinet.

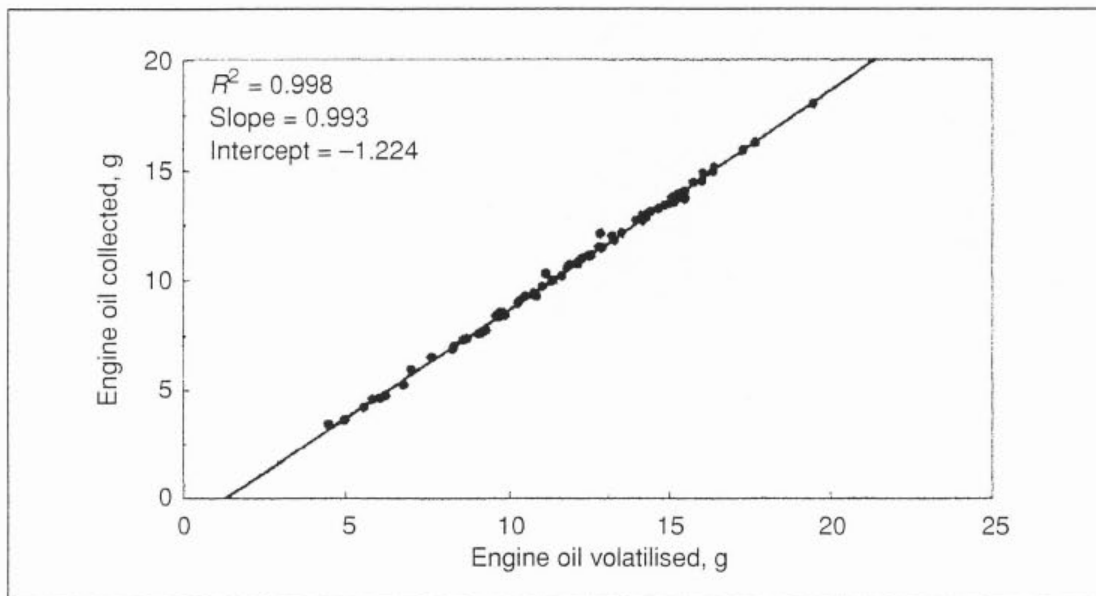
When the three glass components are firmly clamped, the air inlet tube is inserted through the centre ground glass joint to the proper depth. Similarly, the thermocouple tube and thermocouple are put in place. The vacuum control is set to the proper value and both vacuum lines are attached, one to the cap for vacuum control, and the other to the receiver vessel.

If desired, the temperature of the oil in the volatiliser and the vacuum in the cap can be monitored by either a computer or a strip chart.

Operation When the vacuum lines are attached, the test is begun by simultaneously switching on the vacuum pump and the heater. At some point the receiver will begin to collect volatile product.

Figure 2 Correlation of weight of engine oil volatilised and weight of volatiles recovered

(data and engine oils obtained from Institute of Materials database and engine oil repository with permission)



Termination of test and measurements The test terminates in one hour and vacuum and heat to the sample are immediately shut off.

After the volatiliser is allowed to cool, it is weighed and the tare subtracted to obtain the percentage of oil volatilised. In the same manner, the receiver is weighed and the tare subtracted to get the amount of recovered volatile product.

Recovery level for volatiles Early development work with the Selby–Noack approach showed relatively low levels of recovery of volatiles, not enough to allow conclusions to be drawn based on the total volatiles. Consequently, much effort was made to increase markedly the percentage of recovered volatiles.

This work was successful: the amount of oil accounted for is approximately 99% or more if the amount of oil clinging to the glassware is taken into account – about 1.25 g. A small amount of oil is passed through – about 0.02 g – in each test. This oil is trapped by a downstream zero-pressure-drop absorber to protect the vacuum pump.

The recovery rate of volatiles at all levels of volatility is demonstrated by the consistency of recovery in a random selection of 67 tests on engine oils whose volatilities ranged from less than 5% to almost 20%, and included both straight and multigraded engine oils. The results are shown in **Figure 2**.

The correlation between the amount volatilised and the amount collected is high ($R^2 = 0.998$) and the slope is very near unity (slope: 0.993). However,

Figure 3 Comparison of phosphorus content of volatiles versus amount of oil volatilised for Japanese and North American engine oils
(data and engine oils obtained from Institute of Materials database and engine oil repository with permission)

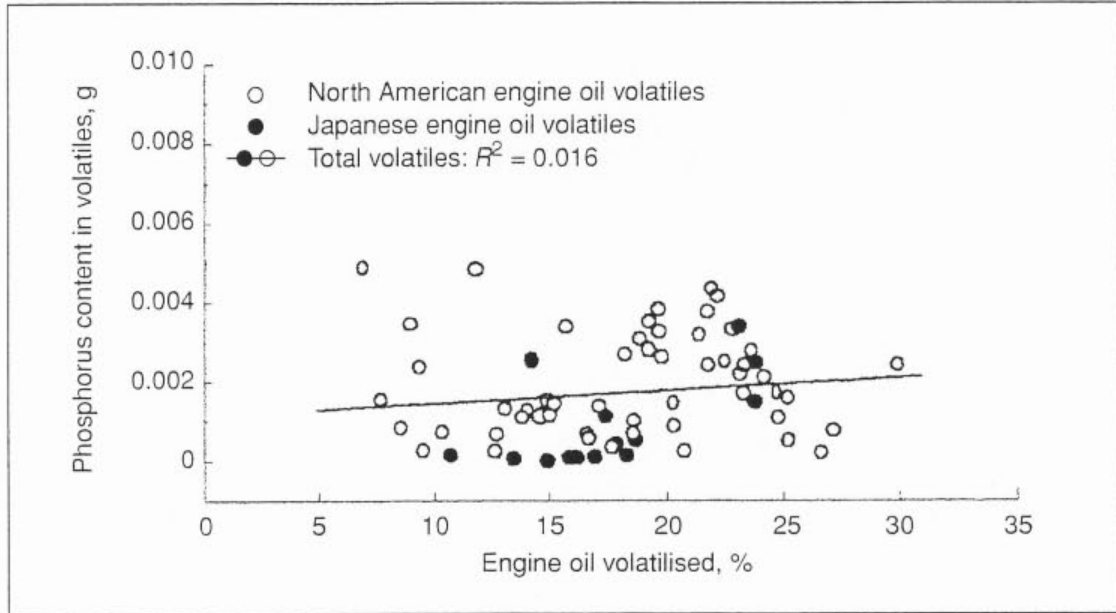


Table 1 Repeatability

<i>Reference oil</i>		<i>Higher volatility oil</i>	
<i>Test</i>	<i>% lost</i>	<i>Test</i>	<i>% lost</i>
1	15.41	1	24.33
2	15.01	2	24.84
3	15.11	3	24.39
4	15.22	4	24.82
5	15.14	5	24.67
Average	15.178	Average	24.61
Std. dev.	0.150	Std. dev.	0.238
% SD	0.99	% SD	0.97

interestingly, the best line does not pass through the origin but intersects the Y-axis at -1.224 g. Investigation showed that the amount of oil still retained in the coalescer and on the glassware is very close to this figure, indicating that all but about 0.02 g are collected either in or before the receiver. That is, about 99.9% of

the volatiles are prevented from reaching the last stage oil absorber before the vacuum pump and, so, essentially no oil reaches the pump itself.

This level of recovery allows confidence in examining the volatiles for their properties as representative of all volatiles produced.

Precision using automatic vacuum control

More recent studies using the automatic vacuum control technique with the Selby–Noack apparatus allow an understanding of the precision of the technique.

Table 1 presents the results of repeatability tests on the reference volatility oil and another reference oil of higher volatility. Results show good repeatability at both levels.

PHOSPHORUS VOLATILISATION

The aforementioned concern with the effect of volatilised phosphorus and the question of the relationship between such volatilisation and overall engine oil volatilisation led to a preliminary study in which the 67 oils used to study volatile recovery were also used to determine the level of correlation between the amount of phosphorus volatilised and the amount of engine oil volatilised. This investigation was thought to be helpful in determining the best way to reduce phosphorus contamination of the emission catalyst.

Both the percentage of oil volatilised (data obtained from IOM database on engine oils) and the phosphorus present by weight in grams of these same oils were cross-plotted. The results are shown in **Figure 3**.

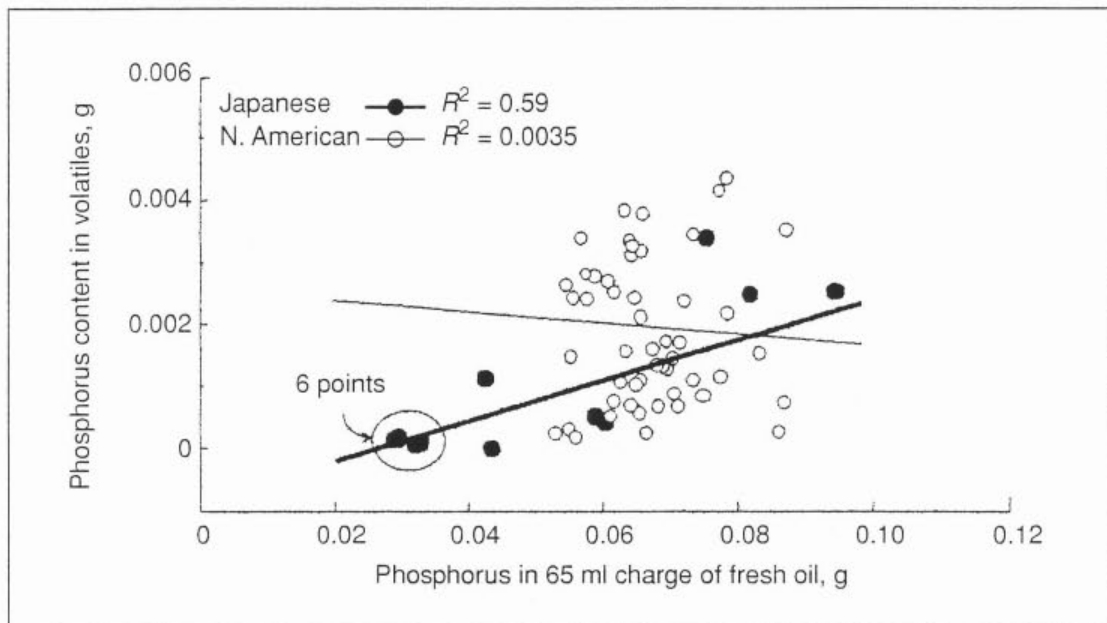
Low engine oil/phosphorus volatility correlation

If there were a close interdependence between the percentage volatility of the engine oil, the percentage of engine oil lost, and the amount of phosphorus volatilised, there would be a high value for the coefficient of determination, R^2 . Instead, the data obtained on oils from two regions of the world show that there appears to be no correlation between the volatility of engine oil and that of the phosphorus in the oil.

Phosphorus availability and volatility

If the amount of volatile phosphorus was not generated by the amount of oil volatilised, what, then, was the cause? This led to the next question, of whether

Figure 4 Comparison of phosphorus content in volatiles versus initial content of phosphorus in fresh Japanese and North American engine oils
(data and engine oils obtained from Institute of Materials database and engine oil repository with permission)



the amount of phosphorus in the original oil dictated the amount of phosphorus volatilised.

Accordingly, the fresh oils producing the results in **Figure 3** were analysed for phosphorus levels. Results are shown in **Figure 4**.

Two observations may be made here. One, in regard to the North American oils, which form the majority of the data, is that there is no correlation between the amount of phosphorus available and the amount volatilised. The slope is actually negative, showing that, if anything, the two concentrations are opposed.

The second observation is that there is a fair level of correlation among the Japanese oils evaluated ($R^2 = 0.56$). The apparent contradiction can be removed if it is the case that the Japanese oils are more alike in the type and amount of phosphorus-containing additives they use.

Both pieces of information suggest that phosphorus-containing additives can, perhaps, be designed to reduce phosphorus volatility.

CONCLUSIONS

This paper has discussed the results from analysis of engine oil phosphorus volatility using the Selby–Noack apparatus. Several conclusions are suggested from the data.

1. Engine oil phosphorus volatility is probably not influenced by engine oil volatility.
2. Engine oil phosphorus volatility may not be influenced by phosphorus concentrations in the engine oil, unless the relationship is founded upon use of the same phosphorus-containing additive.
3. Further studies should be made of the relationship of phosphorus composition and concentration to its volatility.
4. Similar studies should be directed at the time of volatilisation of the phosphorus compounds from the test oil, and how this is related to composition and concentration.

Acknowledgements

The author would like to acknowledge with great appreciation the contributions, insights, and dedication of Richard Hall, Brian Cluff, Andrew Stephenson, Ellie Reichenbach, Dan McMahon, and Larry Schember.

References

1. Drury, C., and Whitehouse, S. Culley, 'The effect of lubricant phosphorus level on exhaust emissions in a field trial of gasoline engine vehicles', SAE paper 94075, 1994.
2. Noack, K., *Angewandte Chemie*, **49** (1936) 385.
3. *Evaporation Loss of Lubricating Oils*, CEC L-40-T-87, 1987.
4. Selby, T.W., Reichenbach, E.A., and Hall, R.H., 'A new approach to the Noack volatility test', in *Proc. 9th Int. Coll. Ecological and Economical Aspects of Tribology*, Technische Akademie Esslingen, 1994, pp. 5.5-1 to 5.5-15; *Tribotest*, **1**, 1 (1994) 3.
5. Selby, T.W., 'Engine oil volatility studies – generation of phosphorus', in *Proc. Int. Trib. Conf.*, Yokohama, 1995.
6. Cluff, B.J., McMahon, D., and Selby, T.W., 'A laboratory method for measuring bulk volatility of engine oils – comparative results', SAE paper 961227, 1996; also in *Engine and Gear Lubricants*, SAE, 1996 (SP 1183).

This paper was presented at the 11th International Colloquium on Tribology, Technische Akademie Esslingen, Germany.

The Tribology Group of the Hungarian Scientific Society of
Mechanical Engineering
and
The Hungarian Chemical Society
invite you to the

7th International Conference on Tribology

4–5 September 2000

at the
Technical University of Budapest

CONFERENCE TOPICS

- Friction and wear •
- Characteristics of surfaces •
- Contact of rubbing surfaces •
- Lubrication of machines •
 - Monitoring •
- Lubrication of engines •
- Industrial lubrication •
- Lubricant additives •
- Lubrication in heavy-duty conditions •
 - Test methods •
- Environmental aspects of tribology •

Official languages: English and Hungarian

Registration fee: USD 120 before 30.06.2000
USD 150 after 30.06.2000 or at Registration

Exhibition fee: - USD 300 (USD 200 for registered participants)

The registration fee includes participation, coffee, proceedings, and the banquet.

Secretariat

Dr. Mihály Kozma, TU of Budapest
H -1111 Budapest, Műegyetem rkp. 3.
Tel: +36-1-463-2363. Fax: +36-1-463-3510.
E-mail: kozma@xenia.gee.bme.hu

Further information from

GTE Rendezvény Iroda
H-1027 Budapest, Fő u. 68.
Tel: +36-1-202-1382. Fax: +36-1-201-7180.
E-mail: berzy.gte@mtesz.hu

Organising Committee

Chairman: Mihály Kozma. Members: Patrick De Baets, László Bartha, András Eleőd, Lajos Kisdéák, Gábor Kalácska, Károly Váradi.