

Vaporisation of oxalic acid and working safety

The search for residues following treatment with oxalic acid for varroa control had been limited to honey and food examinations. To gain more information regarding the working safety for the beekeeper, the Mellifera e.V., Vereinigung für wesensgemässe Bienenhaltung, investigated further questions. The residues of oxalic acid on frames and the by-products of the vaporisation of oxalic acid were examined.

Residues on frames after the vaporisation of oxalic acid

Material and Method

Between 12.12.2000 and 22.01.2001 twelve experimental colonies were treated. Three grams of oxalic acid were vaporised with the VARROX-vaporiser of the company Andermatt BIOCONTROL AG. Five of those colonies had been additionally sprayed with 3 % oxalic acid in the previous November, which exposed them to an additional contamination.

In four intervals, 56 samples of the frames were taken. Since 1991, in the apiary "Fischermühle", each colony was treated at least once a year with oxalic acid, either with the spraying or vaporisation method. The samples were taken from outside frames that were not occupied by bees.

For control, ten samples of different pieces of frames were examined that had never been exposed to an oxalic acid treatment.

With a fine saw, 5 cm² was sawn out of a side strip of the frame. The samples were taken without touching the surface. They were immediately put into a dish and an aqueous solution of the residues was made within 24 hours. The samples were examined with HPLC in an independent laboratory. The lower limit of detection was at 3 micrograms oxalic acid per cm² surface of wood. To examine the dissolving method, the temporal course of the dissolving was documented and a second extraction of previously determined samples was done. The efficiency of the applied procedure was at least 80 %.

Results

Figure 1 shows the content of oxalic acid in the non-treated frames (control) with an average of 8 µg/cm² wood. For comparison, the residues of the samples that were taken in four intervals are shown. Between day 1 and day 27, there is a clear reduction in residues, however the values on days 56 and 96 did not continue this trend. They show a larger scattering of values with some outliers. This variability in the results is currently unexplained.

In one colony (figure 2) samples of five different frames were taken. Two of the frames were in the middle of the winter cluster and were heavily occupied by bees due to the close proximity of brood to the wood. The other three frames were away from the cluster. For each frame, four consecutive samples were taken as shown. Surprisingly, no difference is visible, whether the bees are on the frames or not. But again, there are large irregularities in the values, which are not understandable.

figure 1:

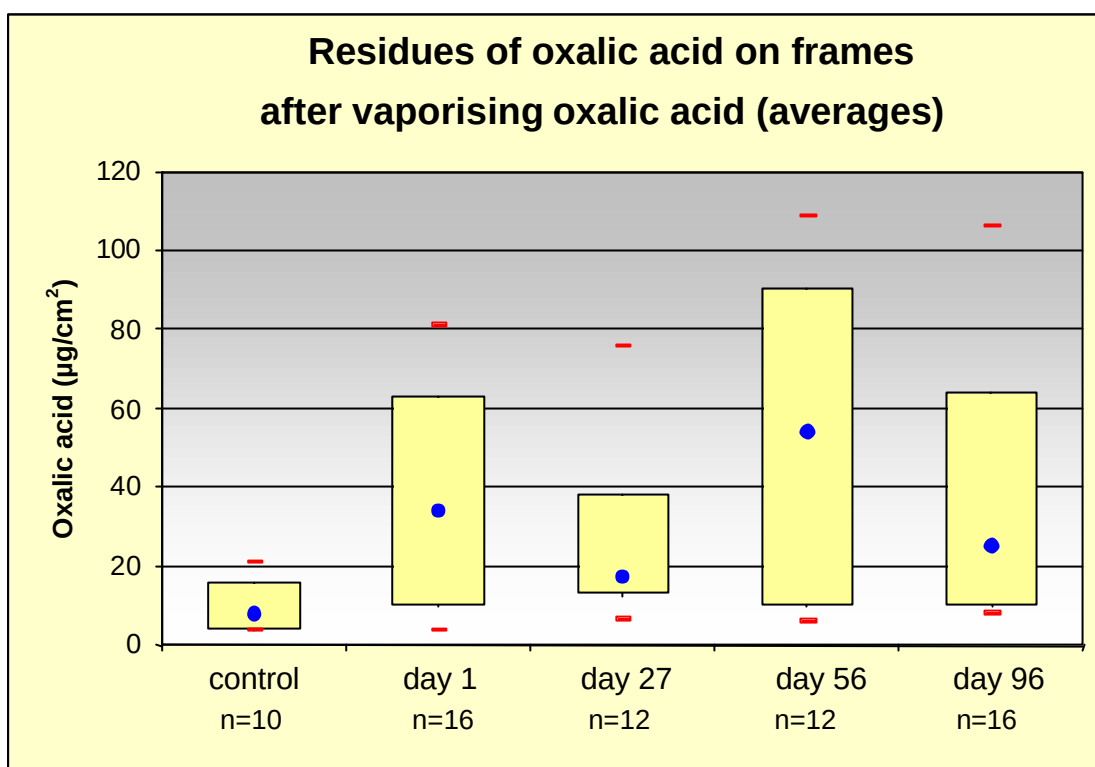
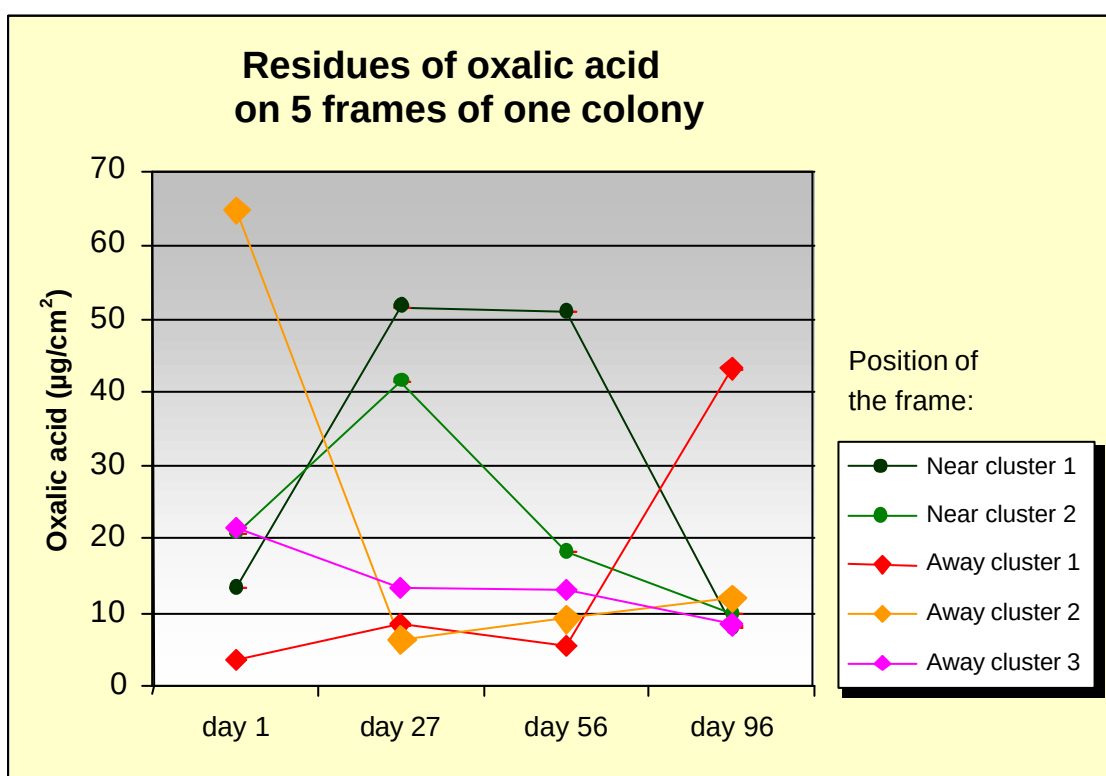
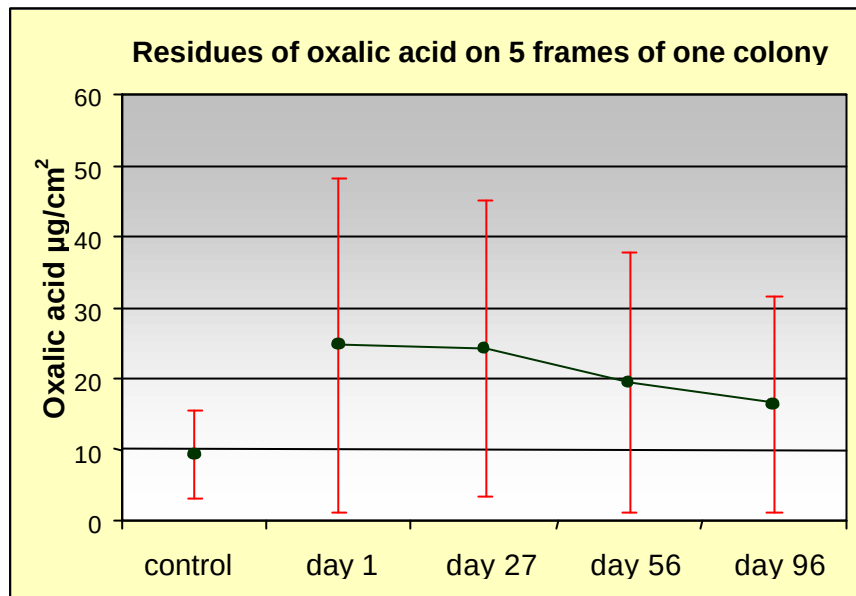


figure 2:



In figure 3 the values of the residues on the five frames are summarised. On the left, for comparison, is the control; on the right, is the course of the average residues during 96 days. These averages and the average of all twelve colonies were still above the residue level in the last control sample.

figure 3:



Discussion

At the moment, the up and downs of the values remain without explanation. As measurements were close to the limit of detection, unavoidable tolerances of the analysis could be of importance. With regard to the total surface on which one can expect precipitation after the vaporisation of oxalic acid, the samples that were taken are only spot checks. An irregular distribution of the precipitation is possible.

The large scattering of residue levels after the treatment may possibly be explained by a difference in previous contaminations. The apiary "Fischermühle" has treated with oxalic acid for over 10 years. To judge the residue data it has to be taken into account that the worst case was examined, the worst situation with the highest possible previous contamination. It could be hypothesised that the wood of the frames is a more or less saturated system. Wood therefore only absorbs a part of the applied oxalic acid.

It is important to mention that the control, consisting of ten samples of non-treated wood of frames, shows a remarkable scattering in the natural content of oxalic acid. Up to the forties wood was used for the extraction of oxalic acid, because it naturally contains oxalic acid.

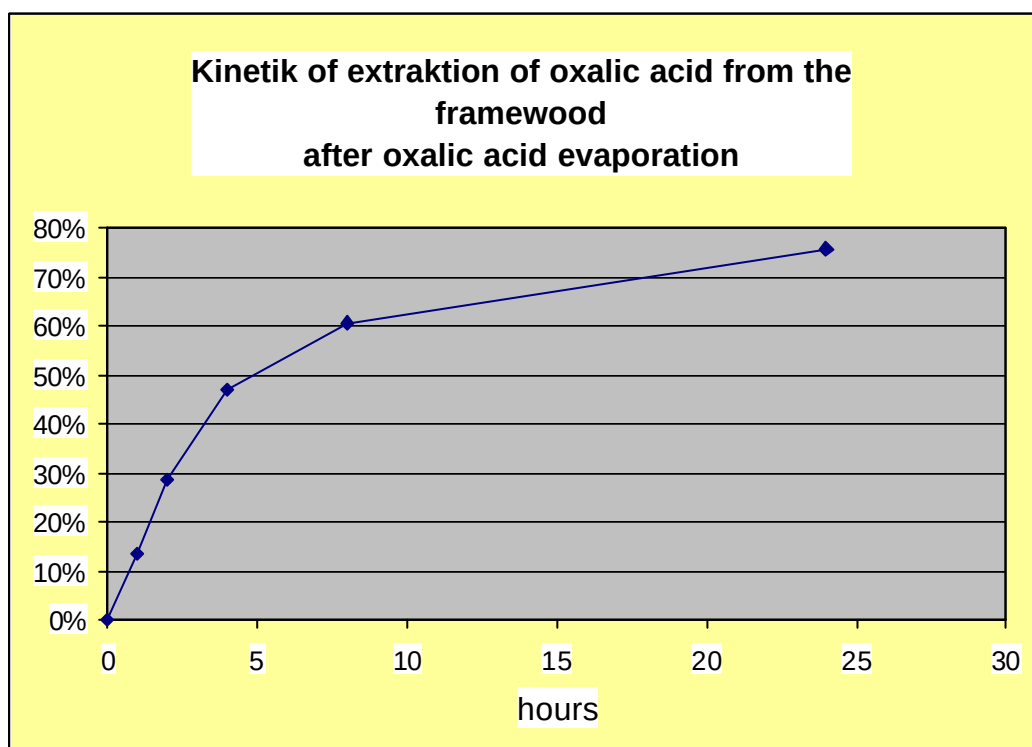
For the toxicological assessment of the results no comparative data of dermatological examinations are known. But from the Austrian Federal Institute for Health Service written information about oxalic acid concentrations in normal trade products is available. Very high amounts of oxalic acid are found in hair cosmetics. According to the information of the above mentioned institute, a maximum concentration of 5 % oxalic acid in hair cosmetics is allowed. Compared to that, the residues in the frames with an insignificant amount of a few micrograms is slightly above the limit of detection.

In the organic bounds oxalic acid is a naturally occurring component of our nourishment. It can be found in almost every plant we eat and it is a natural component of honey in quantities of 0,02 to 0,2 grams per kilogram. Oxalic acid consists of hydrogen, carbon and oxygen (HOOC-COOH).

Rhubarb becomes sour because of 2,6 – 6,2 grams of oxalic acid that is contained in each kilogram of the fresh plant (Macholz 1989). Some pieces of rhubarb – with the same size as the samples of the wood of the frames – were cut and weighed. The pieces contained on average 1,1 mg oxalic acid per cm² (calculated on the basis of a content of 4,4 mg/g oxalic acid). Therefore, the exposure of a housewife to oxalic acid when cutting rhubarb is ten times higher than the highest value that was measured of the treated frames. In comparison with the average residue of oxalic acid of all examined samples the housewife's exposure to oxalic acid is 25 times higher than the beekeeper's.

Furthermore, it can be assumed that the beekeeper's hand is not contaminated with the same amount of oxalic acid that was ascertained in the samples. The oxalic acid is not freely released on the surface of the wood. The above mentioned values of residues refer to the total amount of oxalic acid that was dissolved from the wood in the laboratory within 24 hours. Figure 4 shows how the oxalic acid only gradually dissolves in water.

Fig. 4



Doctoral Thesis for Further Examination of Occupational-Medical Issues

In co-operation with Mellifera e.V., the occupational medical institute of the University of Tübingen will support a doctoral thesis in winter 2001/2002 to further investigate occupational safety. Various data will be gathered from 20 beekeepers. Oxalic acid levels in urine will be measured before, during and after treatment and strain on facial skin and hands will be determined. Moreover, the amount of oxalic acid in the air and particle size will be measured during treatment.

By-products with vaporisation of oxalic acid

In an independent laboratory it was examined which substances arise from the vaporisation of oxalic acid. For that purpose, vaporisation was carried out with the VARROX-vaporiser produced by the company Andermatt BIOCONTROL AG. The arising vapours were sucked into a water bath and the water late analysed. As it cannot be assumed that problematic compounds of higher valency arise they searched for oxalic acid, formic acid, formaldehyde and acetaldehyde. The limit of detection for formaldehyde was at 100 micrograms per gram of vaporised oxalic acid; for acetaldehyde at 80 micrograms per gram oxalic acid.

The amount of formic acid that was found was 1 % of the weight of the vaporised formic acid (10 mg formic acid per gram oxalic acid). Neither formaldehyde nor acetaldehyde were detectable.

By-products	Limit of detection µg/g presented oxalic acid	Found with 1 g vaporised oxalic acid
Formic acid		10 mg
Formaldehyde	100	none
Acetaldehyde	80	none

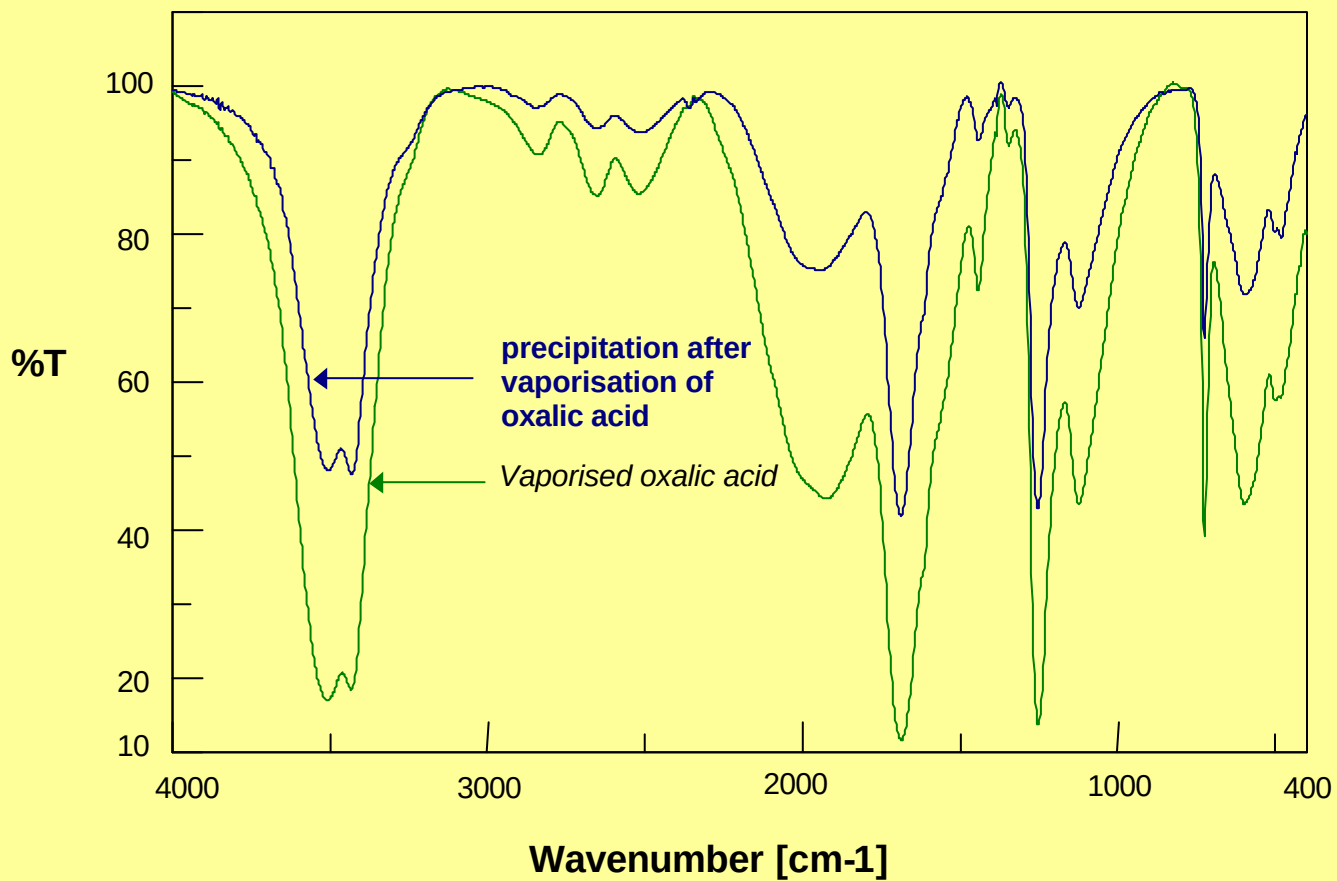
Furthermore, the amount of oxalic acid that is not destroyed through vaporisation but vaporises and precipitates afterwards was examined. With vaporisation of loose oxalic acid crystals, on average 54 % of the used oxalic acid could be found. With vaporisation of oxalic acid in gelatine capsules the rate of finding oxalic acid again was at 34 %. In the large field trial which was carried out by Mellifera e.V. in winter 2000/2001, oxalic acid in capsules was used.

Rate of finding oxalic acid after vaporisation	Average	Single values
Loose oxalic acid dehydrate	54 %	50,7 %; 52,3 %, 58,5 %
Oxalic acid in gelatine capsules	34 %	26,3 %; 35,2 %; 39,2 %

When heating, about half of the oxalic acid decomposes into harmless carbon dioxide and water. The other half vaporises and forms fine drops and dusts of oxalic acid that precipitates everywhere in the hive. Because of the even distribution of these fine particles the high and consistent efficacy against the varroa mite is possible.

Moreover, it was examined if the acid that was found after vaporisation was really identical with the presented oxalic acid. With this aim in view the FT/IR spectrum of the white precipitation after vaporisation was determined. With the “fast fourier transformation with infra-red detection”, the so-called Finger-Print-Technique”, it could be guaranteed that the acid that was found again was identical with the presented acid.

Identification of the precipitation of oxalic acid by means of fast fourier transformation with infra-red detection



Safety precautions for the apiarist

Pure oxalic acid is an unhealthy, toxic and corrosive substance. Therefore, special safety precautions for the beekeeper are necessary, as with other products for varroa control.

With every handling of oxalic acid there is the danger that the dust of the acid is breathed in. The same happens with the preparation of a watery solution for the spraying or trickling method as well as for the oxalic acid vaporisation. A special protective mask (FFP 3 S/L), gloves and protective glasses must be worn. In September 2001, a special tablet was developed for oxalic acid vaporisation which will soon be available in blister packaging. This will allow beekeepers to fill the vaporiser with the exact dose of oxalic acid, without the risk of inhaling the acid. This eliminates contact with the acid.

The low amount of oxalic acid that can eventually escape from the hive through gaps can easily be avoided. During the treatment the beekeeper steps back and pays attention to the wind direction. For security, the mask has to be worn during the treatment. Colonies in a beehouse have to be treated from the outside and the house must be well ventilated during and after the treatment. The amount of oxalic acid that escapes is in any event only a fraction of the amount that surrounds the beekeeper when spraying with oxalic acid. Spray treatment with a 3% solution of oxalic acid is recommended in certain countries; in Switzerland it is part of the official treatment concept. The Swiss Institute for Occupational Medicine and Hygiene in Zurich states, "When performed correctly, treatment with 3% oxalic acid presents no danger to the beekeeper." "...During this procedure, oxalic acid concentrations in the microgram per litre range are produced in the air. Even if this vapour is briefly inhaled, there is no danger of poisoning. Furthermore, since the spray irritates the mucous membranes when inhaled with an open mouth, it causes the user to cough. As a result, even an uncareful user would quickly be reminded when using this biocide to protect eyes, respiratory tract and skin." 9)

It seems legitimate to compare the spray with the vapour leaving the hive. Most of the droplets produced with the spray method have a diameter of a few μm . Mellifera e.V. developed the spray method 4) and performed various tests on it. In the case of the spray method, the oxalic acid is dissipated as so many small droplets that a surface area of up to 4.5 m^2 is produced in a cm^3 of oxalic acid mist. Due to the enormous surface area, the small particles quickly dry to create oxalic acid dust and high-percentage acid. In contrast, with vaporisation, it can be assumed that the condensed oxalic acid particles do not remain dry, but rather immediately bond with humidity in the air.

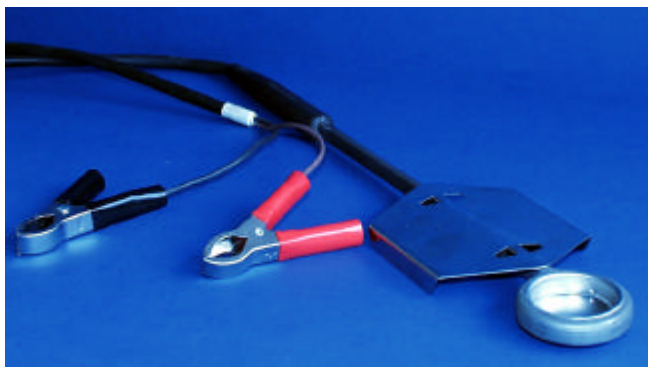
Therefore when spraying or vaporising with oxalic acid a special protective mask (FFP 3 S/L) for solid (=S) and liquid (=L) acidic aerosols should be worn. A normal dust mask from a hardware store is not suitable. The right protective mask as well as the VarroX® Vaporiser, manufactured by Andermatt BIOCONTROL AG, are available in all good beekeeper shops.

Conclusion

According to the presented research results we assume that the application of the vaporisation method is justifiable because the necessary safety precautions can easily be kept. User safety is in every respect greater than that offered by internationally used and recommended spray methods. In terms of handling of the acid, it is even safer than the trickling method if the new oxalic acid tablets are used.

The VarroX® Vaporiser was developed and optimised in the apiary "Fischermühle" to guarantee the application safety and the tolerance by the bees. There is a warning against reproducing the vaporiser, because – apart from the safety risks for the apiarist – the tolerance by the bees and the efficacy is not guaranteed.

A world-wide patent right is pending for the Varrox® Vaporiser and also for the method itself too. The company Andermatt BIOCONTROL AG (address below) has the exclusive distribution rights for the sale of the device.



Addresses



Mellifera e.V., Vereinigung für wesensgemässe Bienenhaltung,
Lehr- und Versuchsimkerei Fischermühle,
DE-72348 Rosenfeld,
Germany,
Phone ++49 (0)7428-935460, Fax ++49 (0)7428-935450,
e-mail info@mellifera.de, www.mellifera.de

Andermatt BIOCONTROL AG,
Stahlermatten 6,
CH-6146 Grossdietwil,
Switzerland, Phone ++41 (0)62 9175000, Fax ++41 (0)62 9175001,
e-mail sales@biocontrol.ch, www.biocontrol.ch

Official Approval of Varrox Vaporiser in Austria

In October 2001 the Varrox Vaporiser and the Varrox tablets were granted official approval in Austria thanks to efforts of the Austrian Beekeepers' Association. Austria is now the first country in the EU in which beekeepers can officially use the method, except during normal honey production times.