Possible Applications of Annealing in Forensic Glass Examinations

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The question that typically arises and requires forensic examinations in connection with crimes involving the breaking of glasses (e.g. burglary, vandalism) is whether the glass fragments recovered from the suspect's clothing can originate from any of the broken objects found on the scene of the crime. A widely used method in the forensic investigation of glass is the refractive index measurement, which – in contrast to the elemental analytical methods e.g. μ-XRF or LA-ICP-MS – can also be applied to fragments in the size range of a few tens of micrometers. If the recovered fragments and the reference have the same refractive index, it is probable that they originate from the same source. These investigations can be supplemented by the heat treatment of the glass samples under controlled conditions followed by the measurement of the refractive index. As a result of annealing, a structural rearrangement takes place in the glass fragments and the refractive index changes. The extent of this change is typical of the glass type due to the different internal stress present in different types of glass. In addition to establishing a more precise relationship of origin, this method also makes it possible to determine glasses by type. Annealing has also been successfully applied in cases where the reference sample has previously been altered by heat or fire during the crime, hence the direct comparison would have given false negative results. The primary aim of this work is to present the results of our experiments carried out at the Hungarian Institute for Forensic Sciences, as well as the possible applications of the annealing of glass fragments in real forensic cases.

Keywords: glass, crime evidence, microtrace, annealing, refractive index, comparative analysis

I. Introduction

The forensic glass examination carried out in Hungary goes back more than six decades, whose brief history, development, as well as the steps and methods of the examination have already been presented.[5] The most frequently asked question in forensic glass examinations is whether there are glass fragments in the clothes or on the objects submitted for testing and, if so, then they can originate from the same source as the reference sample. It primarily means a comparative examination, which can be carried out on the basis of visual color, type, thickness, surface coating, elemental composition, and refractive index (RI) data, depending on the size of the recovered glass fragments. The purpose of this paper is to present an additional examination method, the so called annealing, which, in addition to confirming the results of the comparative tests, makes it possible to determine the type of the questioned glass fragments. Furthermore, it can be used to examine glasses exposed to thermal stress.

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[5] Vörös T., Sándorné Kovács J., 'Kriminalisztikai üvegvizsgálat a Nemzeti Szakértői és Kutató központban', *Belügyi Szemle*, 69 (2020), 177–194.

Depending on the production technology, different types of glass have different levels of internal structural stress. During the production of toughened (safety or security) glass, the pane is heated above the deformation temperature and then cooled down rapidly. This process does not develop the structural equilibrium associated with low temperatures. It results in significant structural stress for this type of glass, which remains in the micro-sized fragments produced during the breakage of the glass pane. If the glass pane is cooled down gradually and slowly during production (e.g. in the case of non-toughened glass), the structural equilibrium corresponding to the low temperature is more likely to develop. The internal stress in the fragments produced during the breaking of such type of glass is much lower compared to that of toughened glass.
The degree of internal stress can easily be checked with the help of heat treatment and subsequent refractive index measurement. During this process, the refractive index of the questioned fragments is measured, and then the fragments are heated above the deformation temperature (approx. 600-650 °C). In this state, a structural rearrangement may take place, and with slow cooling, a significant reduction of the internal stress and a (near) equilibrium state corresponding to room temperature can be achieved, which results in an increase in the RI. The degree of the RI change is related to the original internal stress, thus characteristic of the type of glass from which the fragment originates. In recent years, the examination of the change in the refractive index caused by heat treatment has been successfully applied in several areas. In addition to confirming the results of comparative tests, clarifying the conditions of origin, and determining the type of glass, it also proved effective in comparative tests where the reference glass sample was significantly affected by heat or fire after the glass was broken. In this paper, we would like to present these application possibilities through model experiments and investigations in forensic cases.

II. Glass type determination

The first experiments to distinguish glasses by type using heat treatment were carried out by Locke et al.[6] The refractive index values of 85 glass samples were measured before (RI_{before}) and after (RI_{after}) several hours of heat treatment at 500-550 °C. In their experiments, the RI increment by annealing ($\Delta RI = RI_{after} - RI_{before}$) was approximately 0.00020-0.00150 for non-toughened and container glasses, while for toughened glasses, values between 0.00160 and 0.00220 were observed. Based on their results, the different types of glass – toughened and non-toughened – can be clearly distinguished by heat treatment. This finding was confirmed in several later experiments.[7,8,9] In 2020, the refractive index change of 25-25 container, non-toughened and toughened glasses were examined by annealing at the Hungarian Institute for Forensic Sciences.[10] In these experiments, the fragments of the investigated glass samples were broken into two parts. The refractive index on one was measured, while the other was kept at 700 °C for 4 hours, allowed to cool down to room temperature and then the value of the RI was determined. The measured ΔRI values for each type of glass are listed in Table 1.

[6] Locke, J., Sanger, D. G., Roopnarine, G., 'The identification of toughened glass by annealing' *Forensic Science International*, 20 (1982), 295–301.
[7] Locke, J., Hayes, C. A., 'Refractive index variations across glass objects and the influence of annealing', *Forensic Science International*, 26 (1984), 147–157.
[8] Winstanley, R., Rydeard, C., 'Concepts of annealing applied to small glass fragments', *Forensic Science International*, 29 (1985), 1-10.
[9] Marcouiller, J. M., 'A Revised Glass Annealing Method to Distinguish Glass Types', *Journal of Forensic Sciences*, 35 (1990), 554–559.
[10] Vörös T., Takács K., Réger P., 'Refractive index variations of glass microfragments by annealing – forensic applications', *Journal of Silicate Based and Composite Materials*, 72 (2020), 205–209.

Table 1: The refractive index changes (ΔRI) of 25-25 container, non-toughened and toughened glasses by annealing examined in the Hungarian Institute for Forensic Sciences.

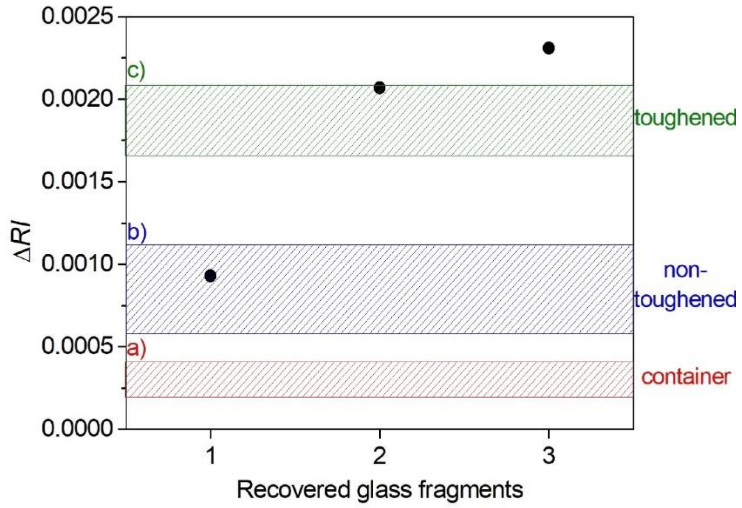
Glass type	ΔRI
container	0.00020 – 0.00040
non-toughened	0.00060 – 0.00113
toughened	0.00166 – 0.00207

It can be observed that the ΔRI ranges do not overlap with each other, which means that the method is suitable for determining the type of glass which the questioned fragment originates from. Annealing can also be used in cases where the investigated fragment is in the few tens of micrometers size range, so the type cannot be determined based on morphological characteristics or by any other technique. In 2022, we had the opportunity to apply the above results in a real forensic case, in which the following question had to be answered: "If glass fragments can be detected on the item of clothing sent for investigation, can it be determined that it comes from a beer bottle?"

Altogether three glass fragments (1-3), in the size range of 100-200 micrometers, were found in the residue of the item after shaking, which were suitable for performing the annealing experiments.

The observed ΔRI values were 0.00093, 0.00207, and 0.00231, respectively. Figure 1 compares these results with the values measured in our Institute on different types of glasses and shows that the questioned fragments cannot originate from a beer bottle. Presumably, one of the fragments is non-toughened, while the other two most likely come from toughened glass. The value of 0.00231 is 0.00024 higher than the refractive index change value of the toughened glasses examined by us, but it is important to note that such a large ΔRI value can occur with tempered glasses based on previous literature data.[11]

Figure 1: The refractive index changes (ΔRI) of 25-25 container (a), non-toughened (b) and toughened (c) glasses by annealing examined in the Hungarian Institute for Forensic Sciences, as well as the appropriate ΔRI values of three (1-3) recovered glass fragments examined in a real forensic case.



[11] Locke, J., Rockett, L. A., 'The application of annealing to improve the discrimination between glasses', *Forensic Science International*, 29 (1985), 237–245.

III. Examination of origin

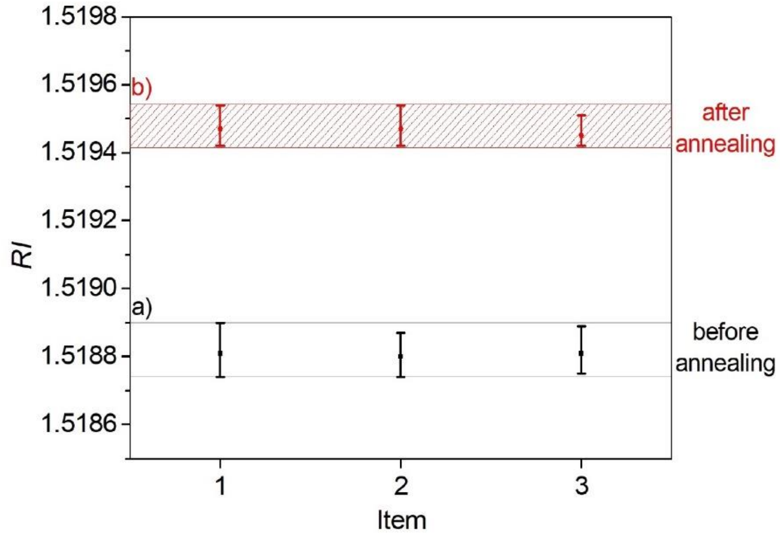
The primary aim of forensic glass investigation is to establish the relationships of origin, if possible, based on the results of several independent test methods. In these cases, we look for properties that can be easily examined both on the reference sample and on the recovered fragments, which typically fall into the micro-sized range (<1 mm). Among the comparative techniques already mentioned in the Introduction, these fragments are primarily suitable for refractive index measurements only, as further comparative examination with an independent method (e.g. determination of elemental composition) is not possible due to their small size. The refractive index can be measured with an accuracy of five decimal places. Based on our measurements, the standard deviation values in the case of glass fragments are typically around 0.0001 or higher, so a more precise measurement than the one currently used is not necessary. However, there are significantly more glass objects in the world than the number of possible different measurement data.[12] It follows that if the refractive index of two glass fragments is the same, only a certain degree of probability of origin can be established, not a categorical match. One way to determine the possible origin more precisely is to compare the RI after annealing and it was successfully applied in the examination of the glass samples of the CTS (Collaborative Testing Services) proficiency test No. 20-5481.[13] In this test, it was necessary to determine whether the recovered fragments marked as Item 2 and Item 3 could originate from the broken glass aquarium represented by the control sample marked as Item 1. Many parameters including the color, type and thickness of the glass fragments, as well as their refractive index and elemental composition measured by X-ray fluorescence analysis were the same for the three items. In order to confirm the possibility of origin from the same source, each fragment was kept in a furnace at 650 °C for 4 hours, and then they were slowly cooled back to room temperature. The RI values measured before and after the heat treatment are presented in Table 2 and Figure 2. It can be observed that the data measured after the heat treatment also support the origin from the same source and are consistent with the results of other examinations. Based on the change in the refractive index values and the data in Figure 1, it can also be seen that all three investigated items are probably pieces of a non-toughened glass.

Table 2: The average, minimum, and maximum RI values observed for Items 1-3 of the CTS proficiency test No. 20-5481 before and after annealing, together with the differences of the average RI values.

Item	Before annealing			After annealing			$\Delta RI_{avg.}$
	$RI_{avg.}$	$RI_{min.}$	$RI_{max.}$	$RI_{avg.}$	$RI_{min.}$	$RI_{max.}$	
1	1.51881	1.51874	1.51890	1.51947	1.51942	1.51954	0.00066
2	1.51880	1.51874	1.51887	1.51947	1.51942	1.51954	0.00067
3	1.51881	1.51875	1.51889	1.51945	1.51942	1.51951	0.00066

[12] Lambert, J. A., Evett, I. W., ‘The refractive index distribution of control glass samples examined by the Forensic Science Laboratories in the United Kingdom’, *Forensic Science International,* 26 (1984), 1–23.
[13] Glass Analysis Test No. 20-5481 Summary Report. Online: https://cts-forensics.com/reports/

Figure 2: The average, minimum and maximum RI values observed for Items 1-3 of the CTS proficiency test No. 20-5481 before (a) and after (b) annealing.

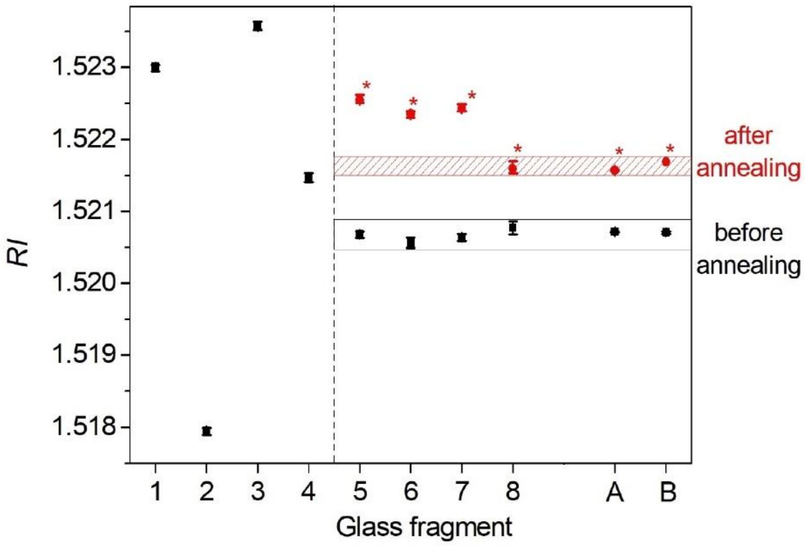


In addition to increasing the degree of probability of origin from the same source, the refractive index measurement, together with annealing can also be suitable for distinguishing between glasses from different sources, but originally with the same refractive index. In a case investigated at the HIFS in 2019, eight reference samples from different broken windows of a motor vehicle were sent by the authority. Among these, the RI values of four control samples (1-4) were clearly different from each other and also from the further control samples, while the RIs of the other four samples (5-8) were very close to each other. Two glass fragments (A and B) were found in the residue of the questioned piece of clothing whose RI values were similar to the control samples 5-8, so their origin could not be clearly determined. To establish the conditions of origin more precisely, each piece of the control samples, as well as the fragments A and B, were subjected to heat treatment at 650 °C for 4 hours, and then, after slow cooling, their refractive index values were measured. It can be seen both in Table 3 and in Figure 3 that control sample number 8 can be clearly distinguished from the samples numbered 5, 6 and 7, since in the former case, the change in the RI due to heat treatment is 0.00082, while for the other three glass samples, the ΔRI values are between 0.00179 and 0.00187.

Table 3: The average, minimum, and maximum RI values observed for eight control samples (1-8) and two recovered fragments (A-B) in a real case before and after annealing, together with the differences of the average RI values.

Glass fragment	Before annealing			After annealing			$\Delta RI_{avg.}$
	$RI_{avg.}$	$RI_{min.}$	$RI_{max.}$	$RI_{avg.}$	$RI_{min.}$	$RI_{max.}$	
1	1.52301	1.52295	1.52304	not investigated			
2	1.51795	1.57189	1.51799				
3	1.52357	1.52352	1.52364				
4	1.52146	1.52141	1.52153				
5	1.52068	1.52063	1.52072	1.52255	1.52251	1.52262	0.00187
6	1.52056	1.52049	1.52064	1.52235	1.52230	1.52239	0.00179
7	1.52064	1.52059	1.52069	1.52243	1.52239	1.52249	0.00179
8	1.52077	1.52068	1.52086	1.52159	1.52153	1.52170	0.00082
A	1.52072	1.52071	1.52072	1.52159	1.52158	1.52160	0.00087
B	1.52071	1.52069	1.52072	1.52169	1.52169	1.52169	0.00098

Figure 3: The average, minimum, and maximum RI values observed for eight control samples (1-8) and two recovered fragments (A-B) in a real case before and for the fragments 5-8 and A-B after annealing (these values are marked with an asterisk).



The measured ΔRI values are consistent with the data in Table 1 and Figure 1, control samples 5-7 were toughened glasses, while sample 8 was a piece of a laminated glass from the vehicle's front windshield. By using annealing, the latter was clearly distinguished from the other samples in our investigation.

IV. Examination of glasses exposed to heat

As a result of heat treatment, the refractive index of glass can change significantly. Under properly controlled conditions, the degree of change can be well reproducible and therefore, it can also be used in forensic investigations. However, in cases where the glass is subjected to a significant thermal shock and the cooling below the deformation temperature is quick, the change in the RI depends greatly on the conditions, and its extent can be significantly different even for glasses from the same source. For this reason, in crimes where the suspect sets fire to the object (e.g. a car or a real estate) after breaking its window, the RI of the recovered glass fragments may differ greatly from the control sample recorded after the fire has been extinguished. Thus, a direct comparison based on the RI may result in false exclusion. Our experiments carried out with toughened, non-toughened and laminated glasses exposed to fire showed that a possible solution to the above-mentioned problem is annealing which means a well-conditioned heat treatment followed by slow cooling to room temperature. Based on the results of a total of 38 experiments with 11 different glass samples, after 4 hours of heat treatment at 650 °C followed by slow cooling, a given glass sample reaches the same refractive index value, regardless of the degree of prior heat exposure, while glasses with originally different refractive indices after controlled heat treatment will also be distinguishable.[14]

These results were also verified with additional model experiments. A pane of a toughened and a non-toughened glass was broken, and 2 fragments smaller than 250 micrometers and 2 fragments in the 250-500 micrometers size range were selected, which are in the typical range

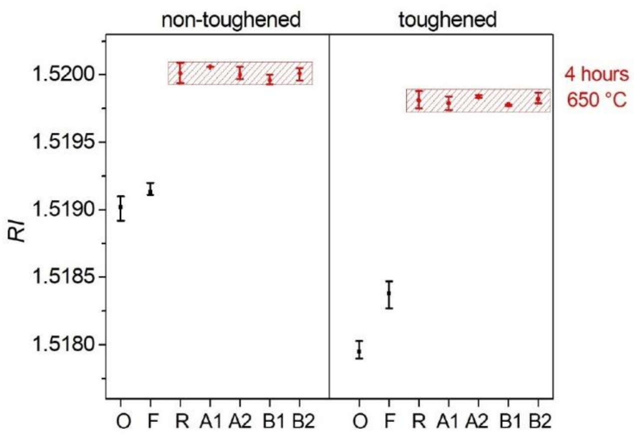
[14] Vörös T., Takács K., Szabó A., Krizsán A., 'Forensic investigation of glass microfragments exposed to heat', *Forensic Science International*, 334 (2022), 111265.

of the fragments that can be found on the suspect's clothing.[15] The remaining part of the broken glass panes were placed in the trunk of a vehicle, which was then set on fire. After 25 minutes of fire, the vehicle was extinguished with water, and reference samples were recorded from the panes. Examining the data in Table 4 and Figure 4, it can be seen that the RI values of both types of glass samples changed to such an extent that the range of the refractive index values measured after the fire and in the initial state were different from each other. It means that the reference sample recorded after the fire and the fragments from the same panes of glass before fire cannot be classified into the same group based on the refractive index. However, after annealing, their RI values match each other within the margin of error, so, by using this method, the relationship of origin can be verified. In Table 4 and Figure 4, it can also be observed that the refractive index of glass samples with originally different refractive index values also differs after heat treatment. The measured average refractive index change in the case of non-toughened glass is 0.00099, while in the case of toughened glass it is 0.00186, which corresponds to the results related to the determination of the glass type.

Table 4: The average (RI_{avg}), minimum (RI_{min}), and maximum (RI_{max}) refractive index values observed for a non-toughened (NT) and a toughened (T) glass in their original state (O) and after 25 minutes of fire treatment (F); furthermore the appropriate values observed for the 2 fragments smaller than 250 micrometers (A1-A2) and 2 fragments in the 250-500 micrometers (B1-B2) and the reference sample (R) after annealing.

Glass type	RI	Original state (O)	After fire (F)	Annealed (4 hours at 650 °C)				
				Ref. (R)	<250 µm		250-500 µm	
					A1	A2	B1	B2
NT	$RI_{avg.}$	1.51902	1.51913	1.52001	1.52006	1.52000	1.51996	1.52001
	$RI_{min.}$	1.51892	1.51911	1.51994	1.52006	1.51997	1.51993	1.51996
	$RI_{max.}$	1.51910	1.51920	1.52009	1.52006	1.52006	1.52000	1.52005
T	$RI_{avg.}$	1.51795	1.51838	1.51981	1.51979	1.51984	1.51978	1.51982
	$RI_{min.}$	1.51790	1.51827	1.51975	1.51974	1.51983	1.51977	1.51979
	$RI_{max.}$	1.51803	1.51847	1.51988	1.51984	1.51985	1.51978	1.51987

Figure 4: The average refractive index values together with the RI ranges observed for a non-toughened (NT) and a toughened (T) glass in their original state (O) and after 25 minutes of fire treatment (F); furthermore the appropriate values observed for the 2 fragments smaller than 250 micrometers (A1-A2) and 2 fragments in the 250-500 micrometers (B1-B2) and the reference sample (R) after annealing.



[15] Vörös T., Takács K., 'Refractive index measurement of the smallest bulk and surface glass microfragments in a model case', *Journal of Forensic Sciences*, 66 (2021), 1948–1955.

V. Summary and conclusions

The forensic examination of glass microfragments in the size range of a few hundred micrometers – similarly to many other forensic institutes – is primarily carried out by refractive index measurement at the Hungarian Institute for Forensic Sciences. The biggest advantage of this method is that it can be used in cases where the measurement of the elemental composition is not possible of the questioned fragments due to their small size. On the other hand, its disadvantage is that it provides only one physical parameter as a result. Given that there are far more glass objects that can be linked to crimes than the number of possible different measurable refractive index values, only a certain degree of probability of origin can be established based on the RI measurement, not a categorical match. In addition, the type of glass – which can be important information in the case of a crime – cannot be determined from the refractive index value. Depending on the production process, different degrees of internal, structural stress are present in the glass, which affects the refractive index. If the investigated fragment is subjected to a well-controlled heat treatment, the stress changes, which is accompanied by a change in the sample's refractive index. The extent of the change that occurs in this way provides additional information about the examined fragment. In accordance with previous results, on the basis of the experiments carried out at HIFS, the change in the refractive index caused by heat treatment falls into clearly distinguishable ranges for container, non-toughened and toughened glasses. Thus, it can be clearly determined whether the glass fragment found at the crime scene comes from a container (e.g. beer or wine bottle), the glass of a property window, or even the windshield of a car door. In addition to type identification, the change in the RI caused by annealing is additional information to the refractive index measured in the original state. It can confirm the assumed origin relationship and can clarify cases where several control samples of different types but with the same refractive index were sent to investigation. The refractive index of glass may change if the control sample is exposed to heat (e.g. fire). In such cases, the RI of the recovered fragments from the suspect's clothing differs from the refractive index of the heat-treated control sample, and their direct comparison results in false exclusion. However, based on the results of our model experiments, by using annealing, it is possible to compare the control sample and the recovered fragments from the same source, even in these cases. In addition to the glass investigating methods used in our Institute, we have successfully applied annealing, thus helping to answer questions related to criminal cases.

VI. References

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