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Dedicated to Professor Emil Cordoș
on the occasion of his 80th anniversary

COMPARATIVE STUDIES BETWEEN CLASSICAL AND MODERN SAMPLING TECHNIQUES TO IDENTIFY THE CONTAMINANTS FROM ENTOMOLOGY ITEMS

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ABSTRACT. Preservation of old entomology items, although very important, is very difficult due to the contamination which they were subjected. In order to test the items contamination level with the classical sampling method, one must be very careful because they are very easily to break and can develop mold spores due to the moistening. The subject of this study is to recreate in the laboratory the stages of preserving the entomology samples by using petroleum products and naphthalene. Then the samples are subjected to two types of sampling, the classical sampling and a new sampling using a special pump for air sampling. After a month in which the items were kept in controlled environment, the sampling procedure was performed and the sample were analyzed. The results showed differences in the results obtained by two sampling techniques. The classical method proved to be more efficient but the items which were studied presents several defects.

Keywords: *sampling procedure, museum, entomology items, naphthalene, total petroleum hydrocarbons*

INTRODUCTION

Many museums and academic institutions maintain first-rate collections of biological materials [1]. These biological collections make innumerable contributions to science and society in areas such as: homeland security, public health and safety, monitoring of environmental change, and

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traditional and systematic taxonomy [1]. For these reasons, the preservation of these collections is very important. The key to long-term preventive conservation in natural history collections is to control the collection environment [2]. Although, nowadays, the biggest museum have implemented integrated pest management techniques or have created new museum spaces with very strict environmental conditions, there are a large number of museum which, despite the current evidence that the use of chemical is declining, are still using pesticides for collection vulnerable to pest activity [3]. “Pesticides” such as: arsenic, mercury, naphthalene, paradichlorobenze and dichloro-diphenyl-trichloroethane (DDT) [3], para-dichlorobenzene, ‘Vapona’ and naphthalene are used since the late 18th century and are still used in some museum [4].

Generally, when talking about museum pollution, museum restorers are thinking about impurities in the environment which may come from natural or man-made source [5]. Their studies are generally focused on airborne sources of pollution, both gaseous and particulate and they are considered to be the primary agents destructive of work of arts [5]. Mainly, the restorers are trying to identify the sources of VOCs, NO_2, SO_2 and O_3 neglecting the pollutants with high impact on human health such as petroleum products (TPH) or naphthalene.

In order to correctly quantify these pollutants a proper sampling is required. In earlier times, the most used procedure for sampling the museum contaminants consists in wiping the surfaces with cotton gauzes wet with distillate water [6, 7]. The procedure described is nowadays generally used for sampling metals such as zinc [8] or for arsenic and mercury based pesticides [9]. In other study, the authors split the pesticides into volatile and non-volatile compounds and the sampling is made accordingly: for volatile compounds they are using solid phase microextraction (SPME) sampling apparatus and for non-volatile compounds they are still wiping the surface of the museum items with cotton swabs [10]. Besides these procedures (active sampling), there are several others procedures which can allow to investigate the accumulation of the pollutants in longer period of time (passive sampling) [11]. The traditional procedure, the wiping procedure, can damage a significant part of museum items comparing to the newer procedures which are safer but more expensive.

This study tried to re-create in laboratory the stages of preserving the entomology samples by using petroleum products and naphthalene. The purpose was to identify a simple sampling method more suitable for entomology items comparing with the traditional one. This sampling method should allow the obtaining of good analytical results without destroying the sample or put it under any risk conditions and, in the same time, to be cheaper than sophisticated methods presented above.

RESULTS AND DISCUSSION

The results obtained for both experiments are presented in Table 1. It can be observed from all data that the value of standard deviation is low. That means that the distribution of the results for every sampling is close to the mean.

The following notation will be done: S1 refers to pump sampling technique and S2 refers to classical sampling technique.

Observing the data, there are several relations that can be followed:

1. The relation between the values of TPH obtained with both sampling techniques, for fresh leaves;
2. The relation between the values of TPH obtained with both sampling techniques for dried leaves;
3. The relation between the values of TPH obtained with first sampling technique, for fresh and dried leaves;
4. The relation between the values of TPH obtained with second sampling technique, for fresh and dried leaves;
5. The relation between the values of naphthalene obtained with both sampling techniques, for fresh leaves;
6. The relation between the values of naphthalene obtained with both sampling techniques, for dried leaves;
7. The relation between the values of naphthalene obtained with first sampling technique, for fresh and dried leaves;
8. The relation between the values of naphthalene obtained with second sampling technique, for fresh and dried leaves;

As it can be observed, for both contaminants TPH and Naphthalene, when comparing the same type of leaves (fresh or dried) the values are much lower for S1 comparing with S2. This result can be due to both: the sampling time using S1 is too short, or an interaction between TPH particles and the surface of the leaves is too strong. When comparing different types of leaves, fresh with dried, it can be observed that both S1 and S2 are higher for dried leaves. This could be due to the fact that the contaminants didn't connect with the structure of the leaves as when they were fresh. These results can suggest that the condition (fresh or dried) of the leaves in the moment they are treated is very important for the step of identifying the contaminants. It is supposed that in time, in function of the initial condition of the leaves in the moment of treatment, other chemical interactions can appear such as a possible crystallization of naphthalene which will send to the surface of the leaves also other contaminants.

The main idea which can be drawn until know is that the classical sampling technique is more efficient especially when the treatment was performed on dried leaves, although this sampling method presents a real danger for entomology items.

Table 1. The results obtained for both experiments, according to the sampling technique used on fresh or dried leaves.

No.	TPH				Naphtalene			
	Fresh leaves		Dried leaves		Fresh leaves		Dried leaves	
	S1	S2	S1	S2	S1	S2	S1	S2
1.	8.34	35.7	13.7	140.03	110.25	449.02	129.32	468.38
2.	8.65	34.8	12.98	139.25	115.68	451.06	125.77	471.22
3.	8.02	35.02	13.04	139.36	118.52	449.22	130.21	469.02
4.	7.89	36.03	13.18	140.21	117.69	452.04	124.54	473.51
5.	8.64	35.22	12.88	140.15	112.45	455.88	129.05	465.85
6.	8.54	35.35	13.56	138.26	122.01	450.02	122.01	471.11
7.	7.93	34.97	13.87	140.03	119.38	452.42	128.44	472.32
8.	9.00	35.25	13.22	140.64	114.22	449.83	127.54	469.88
9.	8.12	35.74	13.05	140.32	119.05	447.65	122.92	471.53
10.	7.81	34.88	13.72	139.99	117.89	450.21	122.31	473.22
Mean	**8.23**	**35.23**	**13.20**	**140.03**	**117.79**	**450.11**	**126.65**	**471.16**
StDev	**0.40**	**0.41**	**0.36**	**0.69**	**3.55**	**2.29**	**3.11**	**2.36**

One has been observed, during the performed experiments, that the dried leaves are very sensitive and very easily to break with the traditional method. Also, once dried, the sample is subject to the possibility of developing mold spores.

Several other experiments must be performed to change the traditional method with the pump sampling. For the beginning we are planning to investigate the effect of different time of sampling for S1.

CONCLUSIONS

The study presents the results obtained by two experiments developed with the purpose to find a safer way to determine the contamination levels on museum entomology items comparative to the traditional method.

In order to reduce the possibility of damaging the museum items to be investigated, two experiments were performed. The difference between the two experiments was given by the sampling procedures which were: the classical procedure, consisting in cleaning the items with sterile gauze pad inserted before in distilled water, and the second, consisting in aspirating the items with the sampling pump.

The experiments were performed on fresh and dried leaves contaminated with TPH and naphthalene. The classical sampling method was proved to be more efficient with the known disadvantage, the danger to destroy the items. Also, both sampling techniques were more efficient on dried samples.

The final conclusion to be drawn from this study is that more experiments should be performed, including on real museum items to improve the pump sampling techniques or to find a correlation factor between the two sampling techniques so as to in the future, the classical method to be replaced.

EXPERIMENTAL SECTION

Materials, standards and reagents

Sterile gauze pad acquired from a local drug store and 0.45 μm paper filters acquired from Sensidyne were used for sampling purposes.

BAM-K009 Lubricating oil (type B) was acquired from LGC Standards, Germany. N-heptane Picograde® for residue analysis, n-decane and n-tetracontane were acquired from LGC Standards, Germany. Florisil (60-100 mesh) was acquired from Meck, Darmstadt, Germany. Crude oil was acquired from local market.

PAH Calibration Mix in Acetonitrile was acquired from Supelco. Cyclohexane for HPLC (purity ≥99.9%), Acetonitrile Chromasolv gradient grade for HPLC (purity ≥99.9%) was acquired from Sigma – Aldrich. Naphthalene was acquired from local market. The ultra-pure water was obtained with a Milli-Q water purification system from Millipore.

Extraction methods

In order to extract the Total Petroleum Hydrocarbons (TPH), the paper filters and sterile gauze pads used for sampling were ultrasonically extracted in n-heptane then the extract was purified with Florisil, 60-100 mesh. A volume of 1 μl aliquot of the final solution was injected in the gas chromatograph in splitless mode, using He as carrier gas.

In order to extract the naphthalene, the paper filters and sterile gauze pads which were used for sampling were left for 24 hours in cyclohexane then the extract was purified with Florisil, 60-100 mesh. The remaining solution was dried using a rotary evaporator and then reconstituted with 1mL of Acetonitrile.

Analytical equipment

The sampling was performed using a Gilian GilAir Plus by Sensidyne pump with a flow of 2 ml/min for 2 min.

The TPH analysis was performed with a gas chromatograph (Agilent 7890N) coupled with a flame ionization detector (FID) and equipped with automatic liquid sampler (HP Model 7673) using He as carrier gas and a HP-5 fused silica capillary column from J&W Scientific.

The naphthalene analysis was performed with Perkin Elmer 200 Series High Performance Liquid Chromatograph (HPLC) with FLD detector, using a ZORBAX Eclipse PAH 5µm, 4.6×150 mm chromatographic column from Agilent and a gradient mobile phase of Acetonitril and Water.

Experimental procedure

In order to reduce the possibility of damaging the museum items to be investigated, two experiments were performed. The difference between the two experiments was given by the sampling procedures which were: the classical procedure consisting in cleaning the items with sterile gauze pad inserted before in distilled water, and the second consisting in aspirating the items with the sampling pump.

Experiment no. 1. 20 fresh leaves and 20 dried leaves contaminated on purpose with the same quantity of commercial crude oil were inserted in desiccators for 1 month. 10 fresh leaves and 10 dried leaves were easily cleaned with sterile gauze pad inserted before in distilled water and 10 fresh leaves and 10 dried leaves were aspirated with the sampling pump. The pump was preset to a flow of 2 ml/min. The sampling time (2 min) was given by the capacity of the operator to cover the entire leave. The samples were prepared further for TPH analysis and analyzed according to a previous developed method [12].

Experiment no. 2. 20 fresh leaves and 20 dried leaves were inserted in a controlled environment which was contaminated on purpose with commercial naphthalene were inserted in desiccators for 1 month. 10 fresh leaves and 10 dried leaves were easily cleaned with sterile gauze pad inserted before in distilled water and 10 fresh leaves and 10 dried leaves were aspirated on a filter with the sampling pump. The pump was preset to a flow of 2 ml/min. The sampling time (2 min) was given by the capacity of the operator to cover the entire leave. The samples were prepared further for Naphthalene analysis. The sterile gauze pads and the filters were inserted in distillated water for 24 hours and then the waters were analyzed according to a previous developed method [13].

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