Riksarkivet	Assessment of a NIR spectrometer for surveying plastics				
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Projekt Dnr 9173/2016	Anmärkningar Final Report				

Assessment of a NIR spectrometer for surveying plastics

- a collaborative investigation into the use of the SurveNIR

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Summary

Plastic materials in heritage collections present an increasing preservation challenge as collections grow and include progressively more modern materials. Informed decisions on conservation methods and preventive preservation can only be taken if the objects' material compositions can be correctly identified and there is a need for simple and reliable methods of identifying plastics. In order to survey a collection efficiently and economically, the analytical method of choice should be reliable, portable, comprehensive and fast. Near infrared (NIR) spectroscopy can meet these requirements and is increasingly used in heritage science. [1]

Between 2005-2008, the EU funded a research project called SurveNIR- Near Infrared Spectroscopy Tool for Collection Surveying, where a NIR spectrometer was modified and the accompanying SurveNIR software developed. The system is designed to investigate a range of chemical and physical properties of paper in a fast and non-invasive manner.[2] The Swedish National Archives participated in the project and acquired the instrument. The instrument's software also contains a less extensive application for plastics and one for negatives and film-materials. These applications have to a large extent been untried for collections and there was a need to validate their use.

In a collaborative project between the Swedish National Archives ("National Archives"), the Swedish National Heritage Board ("National Heritage Board") and the Swedish Army Museum ("Army Museum") the feasibility of using the SurveNIR instrument for the identification of plastics in collections was assessed. Questions the project aimed to answer were:

- How reliable is the SurveNIR for plastics identification?
- What are its limitations in regard to the analysis of plastics?
- How user friendly is it and
- What further developments are needed?

Additionally, the project highlighted certain objects or material classes that are in need of particular conservation attention as the testing of the instrument was carried out in combination with condition assessments.

The project was carried out in four stages:

- Introductory workshop and training session on the SurveNIR with the instrument's developer Dirk Lichtblau e.K.
- Testing the SurveNIR at the National Heritage Board with cross-referencing with known samples and FTIR as a reference technique;
- Testing it on selected objects at the Army Museum and
- Testing it at the National Archives, in Marieberg and Arninge.

The project concludes that the SurveNIR is useful for investigations of plastic polymer type provided that its limitations are known and combined with some basic knowledge of plastics materials. The instrument has functioned in a robust manner being portable, fast and easy to use. In the testing on objects at the Army museum and at the National Archives approximately

[1] Richardson et al. 2007; Richardson et al. 2007 (conference paper); Richardson et al. 2008
[2] Trafela et al. 2008; Rohde, M, Lichtblau, D. 2013

80% of the results from the SurveNIR have been categorised as correct, while remaining analyses where assessed as limited mainly due to limitations of the NIR technique or the current software. Its limitations are:

- Black and very dark objects cannot be analysed.
- Very thin transparent layers and highly reflective materials are not possible to analyse.
- Samples cannot be too small for the analysis area of 4 mm in diameter.
- Objects need be of a shape that is possible to fit satisfactorily to the angled window and semi-transparent objects need to be of a shape that allows the positioning of a back reflector.
- The plastics need to have been included in the initial programming of the software, for instance rubbers and formaldehyde resins are not in the plastic application as of this date.
- Some polymer subtype identifications are unreliable, e.g. differentiation between plasticized and unplasticized PVC.
- Some polymer subtype identifications are not included, e.g. differentiation between polyurethane types –ether and –ester.
- Composite materials cannot be identified, e.g. adhesive tapes, textile reinforced resins.

The application for negatives and film materials needs further development in order to provide the basis for decision making for preventive actions. In particular, if states of degradation could be added to the application this would serve as a tool for prioritising within collections of film and negative materials.

At the National Archives the following object classes were highlighted as being in need of further investigation and developments:

- Preservation and conservation techniques for overhead slides and their writing.
- Degradation processes and preventive actions for architectural and engineering drawings.

The SurveNIR could be used by other institutions of cultural heritage in Sweden and the project suggests that a programme for its wider use could be set up. As one of the National Heritage Board’s objectives is to facilitate the access to analytical resources within cultural heritage, the project suggests that the loaning arrangements and training in the instrument will be run by the National Heritage Board.

This project contributes to the strengthening of a collaborative infrastructure for cultural heritage in Sweden.

1.Introduction

Plastic materials in heritage collections present an increasing conservation challenge as collections grow and include progressively more modern materials.[3] Plastics are becoming ever more divers with sophisticated properties and functions, but often not much is known about their long term stability and ageing behaviours. Discolouration, warping, brittleness, cracking, stickiness and off-gassing are just some of the many symptoms that different plastics suffer upon degradation. However, informed decisions on conservation methods and preventive preservation can only be taken if the objects' material compositions can be correctly identified. Experience in assessing plastics according to their visual, haptic and odour characteristics as well as using manufacturers' labels and recycling codes can go some way in identifying polymer types in collections but far from all and there are severe difficulties in reaching conclusive answers. There is a need for simple and reliable methods of identifying plastics.

Preventive conservation measures can be implemented, in some cases, in order to slow down the degradation, but that implies a need for the correct identification of the material type and its degradation pathway. For example, natural rubbers and other materials that degrade by oxidation benefit greatly from storage in low-oxygen environments; cold storage is often advantageous for cellulose derivatives, while this would not be appropriate for heavily plasticised materials or some laminates. Plastics that are known to become soft or sticky with age need to be separated from other objects and supported on non-stick surfaces; off-gassing can be mitigated through ventilation, absorption or containment, if the sources, composition and effects of evolved gasses are known.

1.1 Background

In order to survey a collection efficiently and economically, the analytical method of choice should be reliable, portable, comprehensive and fast. Near infrared (NIR) spectroscopy may offer just that – it is used in many different industries including pharmaceuticals, agriculture and, for example, in the recycling industry for the sorting of polymers. Over the last decade or so NIR spectroscopy has also made its way into the heritage science sector where the possibilities of a non-destructive, non-contact, in-situ analytical method have particular appeal.

Between 2005-2008, the EU funded a research project called SurveNIR- Near Infrared Spectroscopy Tool for Collection Surveying, where a NIR spectrometer from LLA instruments GmbH was modified and the accompanying SurveNIR software developed. The system with its SurveNIR application is designed to investigate a range of chemical and physical properties of paper such as the pH, degree of polymerization, additives and tensile values in a fast and non-invasive manner. The system is commercially available through Lichtblau e.K. The Swedish National Archives ("National Archives"), Preservation Department, participated in the SurveNIR project and purchased the instrument for their conservation laboratories. The software and its application models are under constant development by Lichtblau e.K. and two additional application models have since been purchased by the National Archives: 1) an application for the identification of plastics; 2) an application for the identification of negatives and film-material.

[3] The term "plastics" as used here comprises natural rubbers, semi-synthetic and synthetic polymeric materials.

The Swedish National Heritage Board ("National Heritage Board"), prompted by a request from the Swedish Army Museum ("Army Museum"), has recognised the need for plastics identification in many collections within Sweden and contacted the National Archives suggesting a possible evaluation and development of the use of their NIR instrument. The National Archives regards such a development as beneficial to the preservation possibilities of the collections and a project was developed.

Plastics in archives are increasingly receiving attention as an area of concern for preservation. Their presence in archives as a category of archival materials has been recognised since the 1990s and there are efforts of locating them in archives in order to find preventive measures, for instance within a mapping project at the UK National Archives.[4]

1.2 Obectives and aims

The National Archives, the Army Museum and the National Heritage Board together investigated the feasibility of using the SurveNIR instrument for the identification of plastics in collections. Questions of concern were:

- How reliable is the SurveNIR for identification of plastic type?
- What are its limitations in regard to analysis of plastics?
- How user friendly is it in terms of non-invasiveness, robustness and software usage?
- What further developments are needed?

One of the initial objectives was to expand the instrument's spectral databases using known materials, however, following communications and a training workshop with Lichtblau e.K. it became clear that this was not going to be possible without the purchase of an additional software package (KustaSpec) that would allow the development of analytical models through chemometrics.

Additionally, the survey has highlighted certain objects or material classes that are in need of particular conservation attention. The results from these condition assessments can be found in the document *Assessment of a NIR Spectrometer - Condition of plastic materials The Swedish National Archives, results from spot-checks.*

Through including participants from museum, archive and conservation science, the project also aimed to strengthen the collaborative infrastructure for preservation within the cultural heritage sector.

[4] Keneghan 1991, Ahmon 2012, correspondance Elke Cwertnia and Kostas Ntanos of National Archives, UK

1.3 Organisation

Participants

Swedish National Heritage Board, Department for Conservation

- (MH) Marei Hacke, advisor – conservation scientist
- (GE) Gabriella Ericson, advisor – collections management

Swedish Army Museum

- (CT) Christina Tengnér, conservator
- (JvH) Jeroen Machiel van Halder, conservator

Swedish National Archives, Preservation Department

- (JFM) Johanna Fries Markiewicz, head of conservation
- (JP) Jonas Palm, head of preservation
- (TW) Thea Winther, advisor, conservator, Preservation Department

2.Project description and Analysis

2.1 Timeline

The project was carried out in four main stages:

- Introductory workshop and training session on the SurveNIR with the instrument's developer Dirk Lichtblau e.K.
  (9-10 May 2016, participants: MH, JP, TW)
- Testing the SurveNIR at the National Heritage Board with cross-referencing with known samples and FTIR as a reference technique
  (26-28 July, September 2016 participant: MH)
- Testing it on selected objects at the Army Museum
  (26-30 September 2016, participants: CT, MH, TW, JvH)
- Testing it at the National Archives, in Marieberg and Arninge
  (November 2016, January 2017, participant: TW)

Additionally, FTIR analyses of samples taken from reference materials and selected objects from the collections of the Army Museum and the National Archives were carried out intermittently at the National Heritage Board. Data interpretation and project meetings also took place at times beyond those mentioned above.

2.2 Near Infrared Spectroscopy, SurveNIR and instrumental set-up

NIR spectroscopy uses the range of the electromagnetic spectrum that lies just beyond the visible region (700 – 2500 nm). In that region overtones and combination bands of molecular vibrations can be observed. Those bands are often broad and less well defined than the fundamental molecular vibrational bands observed in mid infrared spectroscopy, such as FTIR. Nevertheless, simple material identification can usually be achieved through wavelength correlation using raw spectra or second derivative data matched with spectral libraries. More sophisticated qualitative and quantitative analytical methods can be developed based on multivariate and principle component analyses, i.e chemeometrics. The software of the SurveNIR presents results based on this kind of chemeometric analysis and programming and the results for the SurveNIR are highly dependent on that the type of material to be identified has been included in chemeometric modelling. Spectral comparisons are possible to perform through the software Kustaspec Light that is available on the instrument computer. However, spectral features vary dependent on the set-up and components of the NIR instrument used and it is usually not possible to run spectral library matches with reference spectra obtained on a different machine.

The SurveNIR instrument comprises a cooled InGaAs detector with 512 pixel, a spectral resolution of 2nm / pixel and spectral range 1100 – 2200 nm. A RGB camera is inbuilt for sample positioning. The available NIR-spectrometer software packages are KustaWIN, KustaSpec Light and SurveNIR.

The SurveNIR software contains at this stage four applications: two for paper: one for measurement at 18°C and a relative humidity (RH) of 40%, and one for 23°C and 50% RH, one for plastics and one for negatives and film materials. For flat materials a standard flat measurement window is used while for plastics and other glossy materials a tilted window (20°) should be used to avoid interference from reflections. The number of measurements to be averaged for each run can be selected freely. The area of analysis is 4 mm in diameter and for each measurement a photograph is automatically taken. For analysis of transparent materials or thin materials a back reflector is provided.

For this project the applications: "Plastics" and "Film and Negatives" were used on average spectra from 1-6 measurements per analysed material collected with the tilted measurement window 20º and using the back reflector when necessary.

2.3 Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR) instrumental set-up

For ATR-FTIR analysis of reference materials and samples from selected objects from the surveys at the Army Museum and the National Archives a Perkin Elmer Spectrum One FT-IR Spectrometer equipped with a Golden Gate® Single reflection Diamond ATR Series Mark II was used. The spectra were collected over the range 4000 cm^{-1} to 550 cm^{-1} using 4 scans at 4cm^{-1} resolution.

3.Results and Discussion

In total over 200 objects or samples were investigated in the surveys with over 400 separate SurveNIR analyses, see table 2. At the National Heritage Board it was possible to compare the results from the SurveNIR instrument to results from FTIR analysis for the same material. This was not possible at the Army Museum or at the National Archives and hence the assumed probability of the results is based on prior knowledge of plastic materials in combination with other indications such as markings. However, for a few instances where it was of relevance to either the assessment of the reliability of the instrument or to the condition assessment, small samples were taken for FTIR analysis. They are listed below under each locality.

Table 2. Samples and objects tested with the SurveNIR at the National Heritage Board, the Army Museum and the National Archives.

Locality	**Surveys**	**SurveNIR analyses**	**samples/ objects**	**Types (examples)**
National Heritage Board	MoDIP	67	45	containers, toys, utensils
	Army samples	53	27	shoes, cloth, containers
	From *Plast-Morgondagens kulturobjekt*	26	26	samples from cultural history objects from the Nordic Museum, Kulturen in Lund and the Army Museum
Army Museum	Storage	49	39	gas masks, measuring rulers, clothes, instruments
	Exhibition	61	29	clothes, containers, shoes
National Archives	Arninge	117	50	drawings, map materials, film, negatives, OH slides and pockets
	Marieberg	51	21	audiovisual media: VHS, audio, magnetic tapes, their containers, negatives, DIA slides

The result by the SurveNIR software for the plastics application is given as *Material type* which states whether it is a *FULL* or *LIMITED Identification* and as Chemical *Physical Parameter* (**CPP**) which states **Group**, **Polymer**, **Subtype** and **Flame retardant**. For example a white high density polyethylene bottle with *FULL Identification* is given Group: *Polyolefine*, Polymer: *PE* and Subtype: *HDPE*. *LIMITED* indicates that there is no recognition of subtype if subtypes are included in the application. If the spectra are of poor quality and not accepted by the SurveNIR software there are no answers listed under CPP and the status is indicated as *N*.

For a list of polymers and their subtypes included in the application see figure 1.

For comprehensive reports from the SurveNIR software from each survey see appendix I.

For details of tests carried out at the National Heritage Board see appendix II.

For details of the surveys carried out at the Army Museum and the National Archives see appendix III.

SurveNIR_APP Plastics_List of Names_160811

Group	Polymer	Subtype	Flame Retardant	Full Name
Acrylate Polymer	PMMA			polymethylmethacrylate
Aromatic Polyether	PPE			polyphenylene ether
Blend	PPE+PS			polyphenylene ether + polystyrene
Cellulose	Cellulose			cellulose
Cellulose Ester	CA			cellulose acetate
	CTA			cellulose triacetate
Halogen Polymer	ECTFE			ethylenechlorotrifluoroethylene (copolymer)
	PFA			perfluoroalkoxyethylene copolymer
	PTFE			polytetrafluoroethylene
	PVC			polyvinylchloride (LIMITED Identification)
	PVC	PVC-P		polyvinylchloride plasticised
	PVC	PVC-U		polyvinylchloride unplasticised
	PVDC			polyvinyldienechloride
	PVDF			polyvinyldienefluoride
Polyamide	PA			polyamide (LIMITED Identification)
	PA	PA6		polyamide 6
	PA	PA6-10		polyamide 6.10
	PA	PA66		polyamide 6.6
Polyaryletherketone	PEEK			polyetheretherketone
Polyester	PBT			polybutyleneterephthalate (copolymer)
	PC			polycarbonate
	PET	PET		polyethyleneterephthalate (copolymer)
	PET	PET-G		polyethyleneterephthalate, glycole modified (copolymer)
	PLA			polylactic acid
	POM			polyoxymethylene
Polyolefine	EPDM			ethylene propylene diene monomer rubber
	EVA			ethylene vinylacetate (copolymer)
	PB			polybutene
	PE			polyethylene (LIMITED Identification)
	PE	PE-HD		polyethylene high density
	PE	PE-LD		polyethylene low density
	PP			polypropylene
Polysiloxane	SI			polysiloxane (silicone)
Polyurethane	PUR			polyurethane
Styrene Polymer	ABS			acrylonitrilebutadienestyrene (copolymer)
	ABS		Mg(OH)2	acrylonitrilebutadienestyrene (copolymer) + magnesium hydroxide
	ABS		TBBPA	acrylonitrilebutadienestyrene (copolymer) + tetrabromobisphenol A
	ABS		TBBPA-ep	acrylonitrilebutadienestyrene (copolymer) + tetrabromobisphenol A epoxy resin
	PS			polystyrene
	PS		TBBPA	polystyrene + tetrabromobisphenol A
	SAN			styrene acrylonitrile (copolymer)
	SB			styrene butadiene (copolymer)
	SB		Mg(OH)2	styrene butadiene (copolymer) + magnesium hydroxide
	SB		TBBPA	styrene butadiene (copolymer) + tetrabromobisphenol A
	Styrene			(acrylonitrile) (butadiene) styrene (copolymer)(ABS, SB, PS or SAN)(LIMITED Identification)

Fig. 1. Table of included plastics 2016 (note: cellulose nitrate is now included though missing from this slightly outdated list)

3.1 At the Swedish National Heritage Board

The SurveNIR instruments “Plastics” application was tested with known reference materials from three sources:

- Museum of Design in Plastics (MoDIP) Identifying Plastics Travelling Toolkit,
- Swedish army samples provided by the Army Museum,
- Reference samples from a previous project of the Swedish National Heritage Board: *Plast – morgondagens kulturobjekt*, 2008.[5]

The MoDIP toolkit contains types of synthetic and semi-synthetic plastics often found in museum collections, excluding textiles. It includes both sample pieces and whole objects, see figure 2 and table 3. The MoDIP toolkit came with detailed documentation for each object and polymer sample and the SurveNIR results were therefore directly compared to the documents with no further cross-checking by FTIR, see figure 3.
The Swedish army samples had partially incomplete material documentation and all samples were therefore cross-checked with FTIR analysis, see figure 4.
Samples from the project *Plast- Morgondagens kulturobjekt* were of a small size, only a few mm in diameter, and the SurveNIR results were compared to the FTIR results as listed in the project publication [6], see figure 5.

Fig. 1. SurveNIR at the Swedish National Heritage Board


Fig. 2. MoDIP travelling toolkit

[5] Nord et.al.
[6] Nord et.al.

Table 3. Plastics included in the MoDIP toolkit

Plastic	**Abbreviation**	**Included in the SurveNIR "Plastics" application**
Acrylonitrile butadiene styrene	ABS	✓
Bois durci		no
Casein formaldehyde		no
Cellulose acetate	CA	✓
Cellulose nitrate	CN	✓
Hard vulcanised rubber		no
High density polyethylene	HD-PE	✓
Low density polyethylene	LD-PE	✓
Melamine formaldehyde	MF	no
Phenol formaldehyde	FF	no
Polyamide	PA	✓
Polycarbonate	PC	✓
Polyethylene terephthalate	PET	✓
Polymethyl methacrylate	PMMA	✓
Polypropylene	PP	✓
Polystyrene	PS	✓
Polyvinyl chloride (plasticised)	PVC-P	✓
Polyvinyl chloride (unplasticised)	PVC-U	✓
Urea formaldehyde	UF	no

MoDiP reference samples

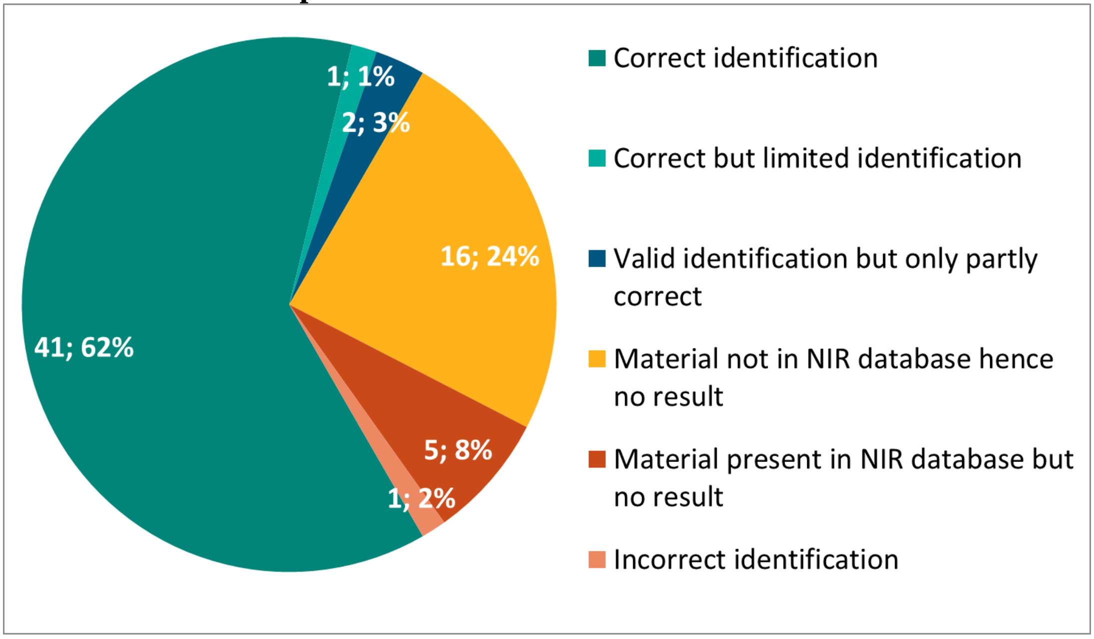

Fig. 3. Comparison of results from SurveNIR and MoDiP toolkit documentation.

The majority of MoDiP toolkit samples (63-66%) were correctly identified. The correct but limited identification refers to a black matt ladle made of polyamide where the subtype was not recognised. The valid but only partly correct identification was obtained for two samples made by bois durci[7], where cellulose was the result stated by the SurveNIR, which is partly correct as saw dust is used as an ingredient. Bois durci itself is not included in the "Plastics" application. Approximately a quarter of the types of materials in the MoDiP toolkit were not included in the SurveNIR "Plastics" application and hence not identified. This is a situation

[7] Ingredients of bois durci are blood, powdered wood and colour.

that is likely to also occur in surveys of plastics in museum and archive collections. These materials were mostly formaldehyde resins and natural rubber.
The quality of obtained spectra from five samples was below the acceptable threshold for the SurveNIR software and hence these samples were not identified even though the relevant polymers were included in the application. They were all of black or very dark colour except for one transparent PET bottle where it was not possible to suitably position the back reflector. Difficulties with black and very reflective materials are known limitations of the SurveNIR instrument, or the NIR technique in general, and need to be taken into account when planning surveys of plastics in collections. The one incorrectly identified sample was a dark brown phenol formaldehyde box which the SurveNIR software stated as polyurethane. This is more troubling than receiving no result, but with some prior knowledge of plastics and their characteristics such unlikely results can be spotted when carrying out a survey.

Army Museum reference samples

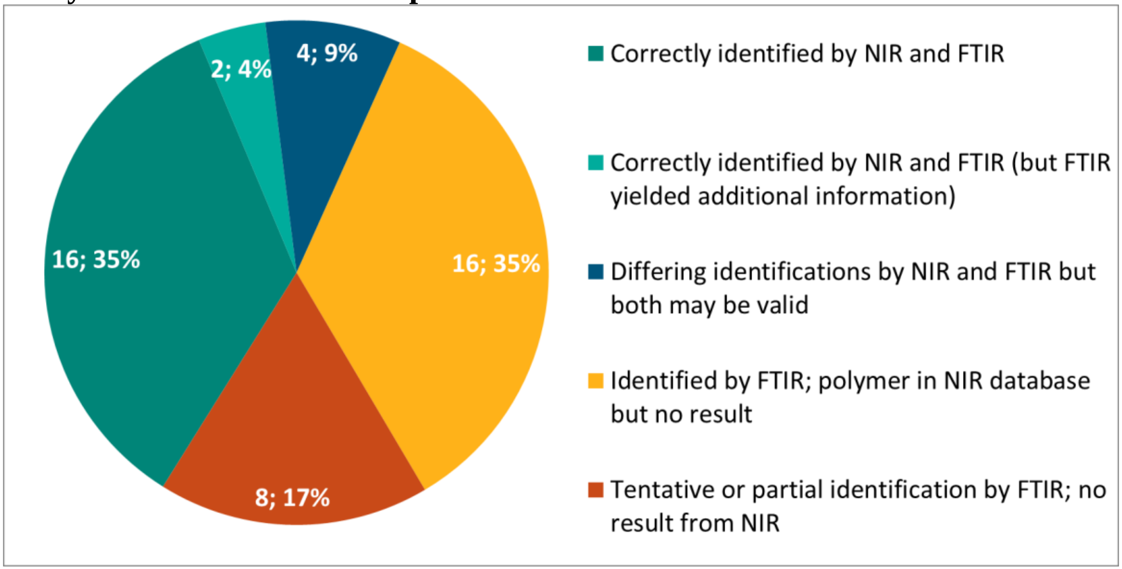

Fig.4 Comparison of results from SurveNIR and FTIR analysis of Army Museum supplies samples.

The materials from army supplies were cross-checked with FTIR analysis and just under half of the samples tested led to correct or valid identifications. The two samples where FTIR yielded additional information refer to cotton polyester blend textiles where the SurveNIR result identified the textiles as polyester whereas the FTIR spectrum clearly showed the presence of both cellulose and polyester. Of the four samples with differing but valid FTIR and NIR identifications, one was a blend fabric of 70% PVC and 30% polyester (Försvarets Materielverks Materialkatalog M7779-603010), which the SurveNIR identified as PVC while the FTIR spectrum was dominated by polyester with some contribution from PVC, see figure 5. Another differing but valid result came from a polyamide textile with an acrylic coating on one side that was identified with FTIR but missed by NIR. This is a known limitation and needs to be considered if coatings or very thin layers are of interest. The deep penetration of NIR means that it is a bulk analysis technique when compared to the surface sensitivity of ATR-FTIR. The other two differing identifications refer to textiles with inorganic fillers where the FTIR spectra were dominated by the inorganic component while the NIR identification pointed to the polymer substrate.

Just over half of the samples from the army supplies yielded no results from the SurveNIR. The sixteen spectra marked as “identified by FTIR but no results from NIR” come from nine samples of different types of coated textiles, such as nylon with a PVC waterproofing. Again, the depth of penetration of the NIR analysis means that the obtained spectra contain features from both the textile substrate and its coating; such composites cannot be distinguished by the software unless they were specifically included in the model for the SurveNIR "plastics" application. The other eight spectra with no result from the SurveNIR also had no or doubtful results from the FTIR spectra; they were often dominated by inorganic components with little indication for the type of polymer.

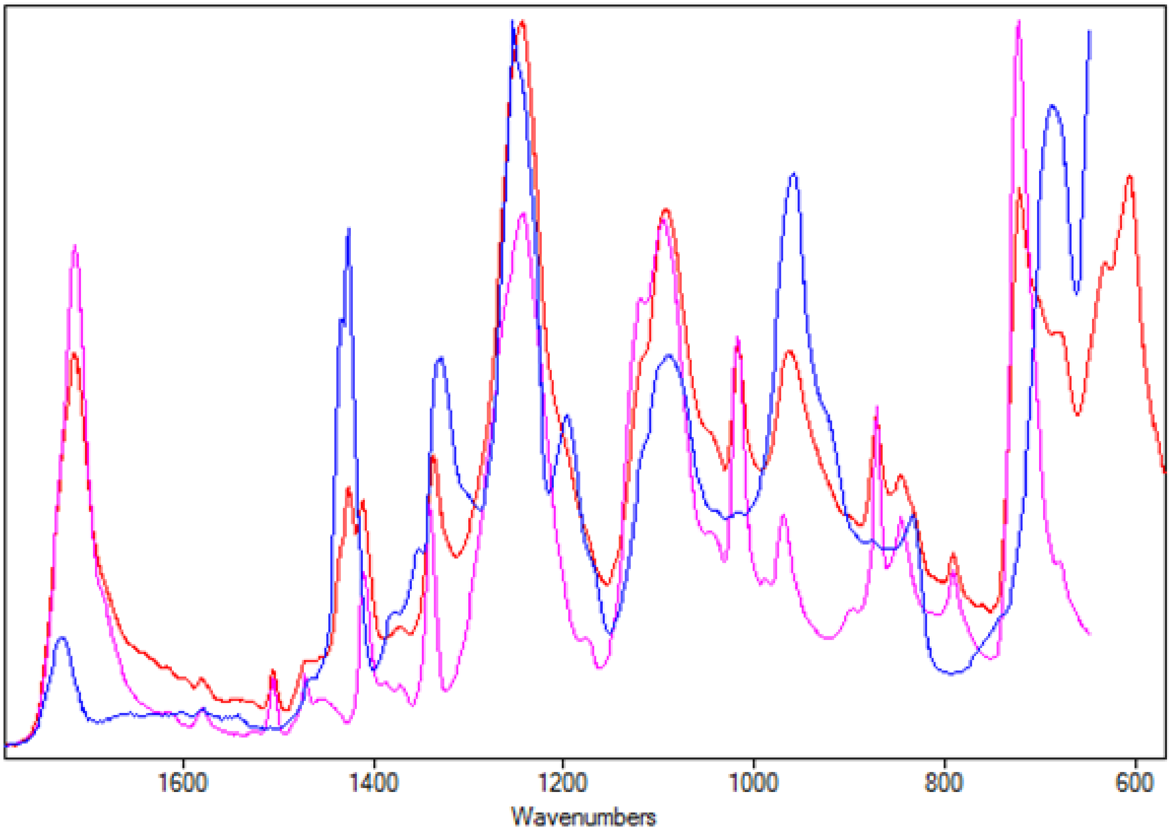

Fig. 5. ATR-FTIR absorbance spectra detail range 1800-600 cm^{-1}: Army Museum reference sample AM18 (undergarment textile); PET (Melinex); PVC unplasticised (1977, no 03 from BRE)

***Plast-Morgondagens kulturobjekt* reference samples**

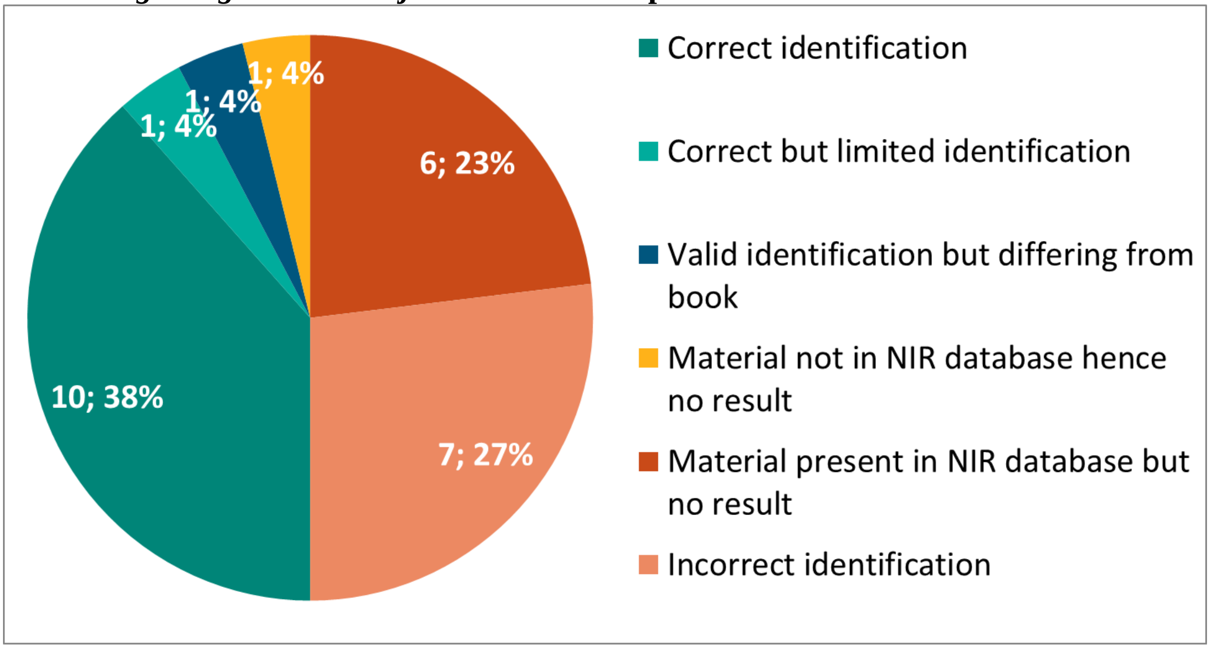

Fig. 6. Comparison of results from SurveNIR and those listed in *Plast-Morgondagens kulturobjekt.*

Less than half of the twenty samples from the earlier plastic project *Plast - Morgondagens kulturobjekt* gave correct results and a quarter of the tested samples yielded incorrect results, see figure 6. The poor performance of the SurveNIR for this sample group was due to the small sample sizes which did not cover the entire measurement area of 4 mm diameter in all cases, see figure 7. The investigation of this reference collection was therefore stopped after only twenty samples.

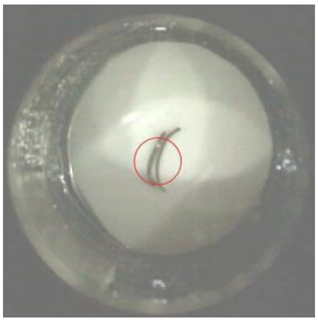

Fig. 7 Samples from project *Plast- Morgondagens kulturobjekt*, small pieces on the measuring window with a red circle marking the area of analysis of 4 mm diameter, SurveNIR camera.

3.2 At the Swedish Army Museum

At the Army Museum several plastic objects of unknown composition were chosen by conservator Christina Tengnér from her prior experience of the collections. This took place both in the storage facilities and in the exhibition area at the museum, see figures 8-9. The aim was to cover a variety of different plastic objects in regard of date, condition, colour, shape (i.e. sheet, foam, cloth etc.) and surface characteristics. The objects investigated in the storage dated mostly from World War I through to the 1970s, while those in the exhibition, which was an army living quarters container came from the 1980s-2000. The SurveNIR identifications were combined with a condition assessment using a form developed by the EU project Preservation of plastic Artefacts in the Museum environment (POPArt). [8] The condition assessment sheets may be attached to the objects' entries in the museum collection data base Primus. Each object was also photographed. 39 objects were studied at the storage and 29 in the exhibition with a higher number of separate SurveNIR analyses as many objects comprised more than one material. The SurveNIR analysis of the objects was fast for most objects, while the condition assessment was quite time consuming. It is worth considering this when planning a collection survey as the available instrument time could be optimised if condition assessments and necessary object documentation are prepared in advance.
The results from the SurveNIR surveys at the Army Museum are shown in figure 10 and detailed in appendix III.

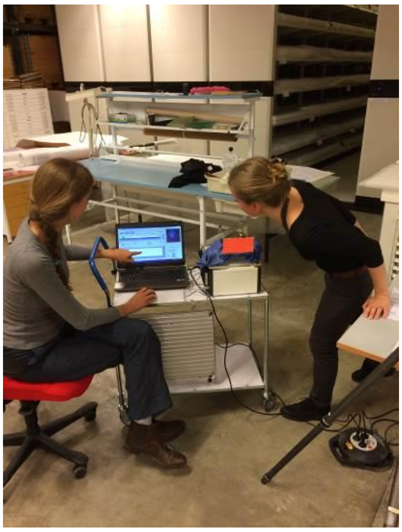

Fig.8. Instrument set-up Frihamnen. Marei Hacke and Christina Tengnér.

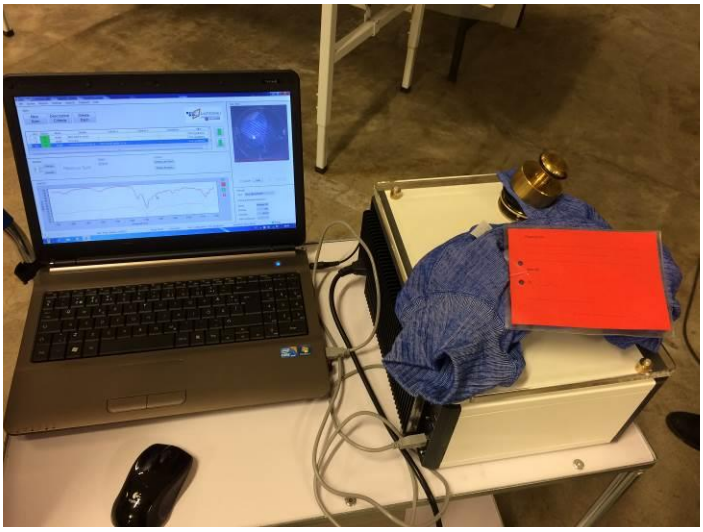

Fig.9 Analysing 1970's under garment.

[8] Collection survey form Preservation of plastic artefacts web page: http://popart-highlights.mnhn.fr/collection-survey/what-is-the-condition-of-the-collection/index.html (2017-02-17)

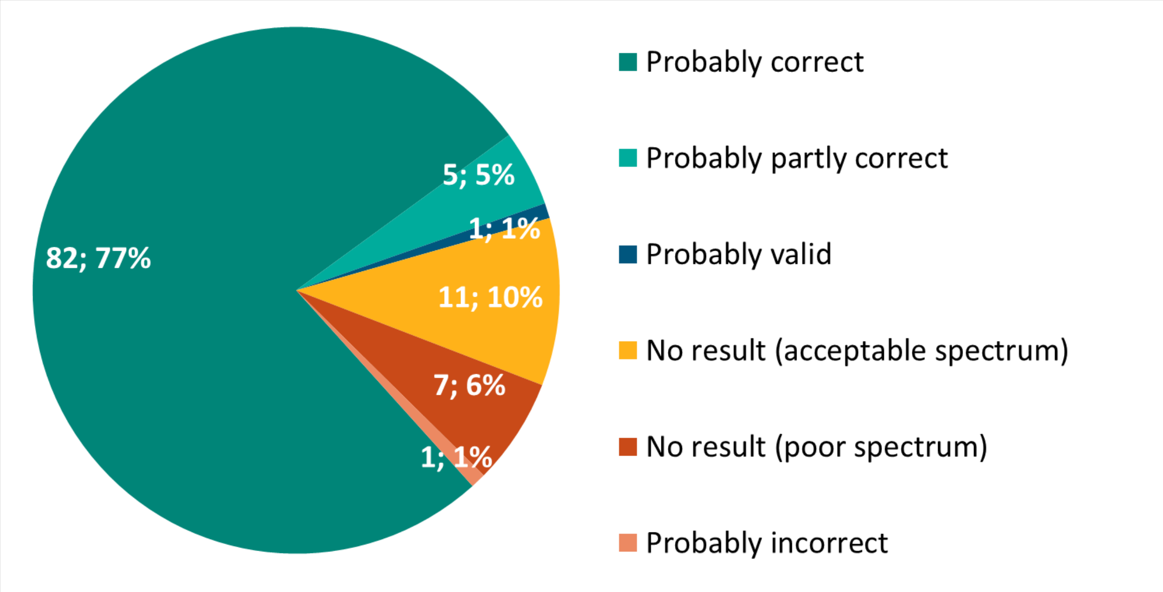

Fig.10. Categorised results from the SurveNIR at the Swedish Army Museum.

Fig.11 Harness

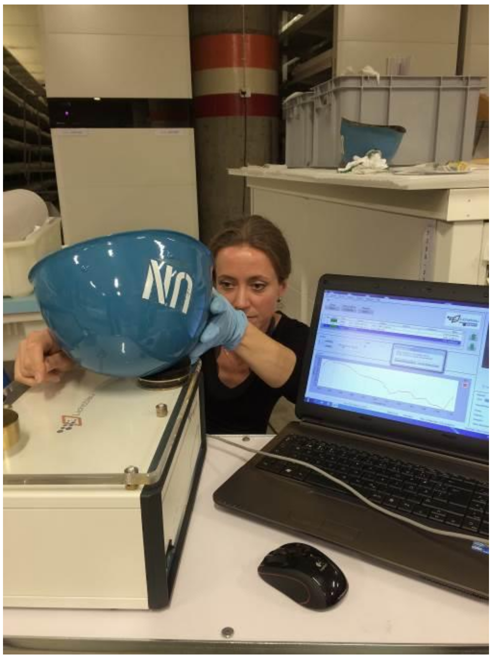

Fig.12. UN helmet

For 77% of the objects tested at the Army Museum the SurveNIR yielded results that are likely to be correct, i.e. see category “Probably correct” in figure 10. A further 6% were deemed probably partly correct; these were results from textile reinforced resins on the insides of UN helmets from the 1950s and 1960s, and PVC materials where the subtype was either unspecified or incorrectly identified. These PVC materials were a blue soft folder, a soft plastic coated textile battle harness (see figure 11) and a gym shoe sole, for the latter two the SurveNIR results were un-plasticised PVC (PVC-U) which is unlikely given the suppleness of the materials. For one material (1%) the SurveNIR result was evaluated as valid, this was a polyurethane coated polyamide textile which was identified as PUR by SurveNIR. Eleven of the tested materials (10%) yielded no results despite the spectra being of acceptable quality. In most instances this was due to composite materials or the polymer not being included in the SurveNIR “plastics” application, but also includes two objects of cellulose acetate. A further seven materials (7%) yielded no results because the obtained spectra were of poor quality; these were mostly from black, very dark or highly reflective surfaces. Only one result (1%) was deemed probably incorrect and refers to a UN helmet where the SurveNIR stated polyamide which was not consistent with the FTIR analysis confirming the material as a semi-synthetic cellulose resin, see figure 12.

Taking the SurveNIR measurements with a back reflector worked well for objects of transparent plastics such as rulers and wind shields for motorcycling, see figures 13 and 14. For a few of the gas masks problems were encountered as it was not possible to insert the back reflector, see figure 15.

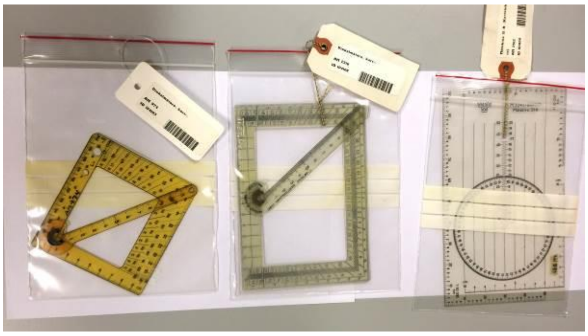

Fig 13. Measuring rulers made of cellulose nitrate, cellulose acetate and polystyrene.

Fig. 14. Motorcycling wind shields made of cellulose nitrate (or cellulose acetate in one case only).

Fig. 15. Gas mask from Verdun WW1 with eye pieces made of semi-synthetic cellulose.

ATR-FTIR

Four objects were sampled and analysed by ATR-FTIR either to compare with SurveNIR results or when the identification was assessed as an important aspect and the SurveNIR gave no answer, see table 4.

Table 4. Objects from the Army Museum analysed by FTIR

Object	FTIR result	SurveNIR result
AM 16888 UN helmet textile and resin reinforced	Cellulose or semi-synthetic cellulose	the SurveNIR gave results for cellulose (AM 16887 and AM707) and polyamide (AM 16888) but FTIR analysis showed that it is not polyamide
AM 16251 ansiktsskydd 1963	Cellulose acetate (very good FTIR fit with cellulose acetate butyrate)	No result
AM 9570 ansiktsskydd modelexemplar	Cellulose nitrate	Cellulose nitrate
AM 77910 gas mask eye piece	Cellulose (or possibly cellulose acetate)	No result

3.3 At the Swedish National Archives

The instrument was tested on a selection of plastic materials in the collections of the National Archive, see table 5 and figures 16-19. Suitable plastic materials were located through searches in the Arkis database with plastic related search words and those results were combined with information from interviews with archivists Ulf Jönson, Roger Munck and Magdalena Salomonsson. The aim was to cover a wide range for spot-tests on materials and condition. The condition assessment sheet from the POPart project was modified into a simpler model in an Excelsheet, see *Assessment of a NIR Spectrometer - Condition of plastic materials The Swedish National Archives, results from spot-checks* and appendix IV.

The material chosen for this survey from the National Archives Arninge comprised one archival box of educational material from Statens hundförarutbildning mainly consisting of hand-drawn drawings on overhead (OH) plastic sheets kept in plastic pockets, engineering drawings for machines and train parts from Statens järnvägar and drawings for buildings from Kungliga Byggnadsstyrelsen from mainly the 1950s – 1980s, films and negatives from Statens maskinprovningar and materials used for making maps from Lantmäteristyrelsen from ca 1978. Materials chosen from Marieberg were mainly audio visual media and their containers. Some extra materials that did not come from a collection were also analysed. For sources with many objects some were chosen for closer inspection to cover variations of the material.

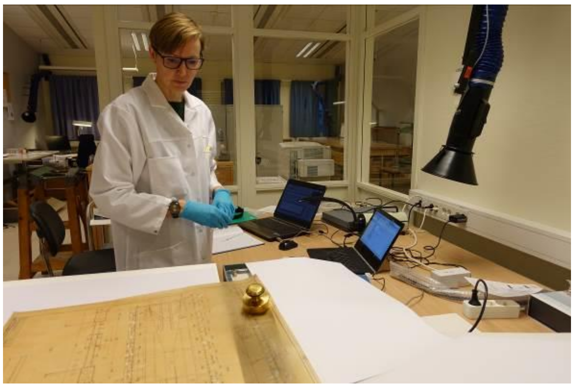
Fig 16. SurveNIR instrument set up at the Swedish National Archives Arninge investigating construction drawing.


Fig 17. SJ Construction drawings in their storage drawer.


Fig 18. Plastic sheets used for production of maps at Lantmäteristyrelsen.


Fig 19. Film 'Malm' from Grängesbergsbolaget

Table 5. Investigated materials from the Swedish National Archives Arninge and Marieberg

Archival source	**Abbr. in SurveNIR files**	**Consisting of**	**SurveNIR separate materials measured in "Plastics" application**	**SurveNIR separate measurements "Negatives and Film" application**
Statens hundförarutbildning	SH	78 OH sheets in pockets, 3 papers in folders	22	
Statens järnvägar maskinritningar	SJ_MR	100 drawings in one drawer, 2 singles	16	
Kgl. Byggnadsstyrelsen	KBS	4 architectural drawings	6	
Statens lantmäteriverk	SLMV	32 plastic sheets for map making, some with tape	15	
Statens maskinprovningar	SMR	3 films, album of negatives with 3 negative strips	1	6
Extra	Plastic examples of damage, polyester films of varied thickness, Secol polyester folder, unknown sample, plastic dia pocket, CD, blue cecolite container (Svenska badmintonförbundets film 1949)		17	
Järnvägsanställdas helnykterhetsförbund, Soligt och roligt i Västerbotten 1946	SJ_SPF130 9	1x 11 mm film		1
De förenade FNL-grupperna, huvudarkivet	DFFG_LG 99	LP-record	3	
Skolöverstyrelsen Våra barn och skolan	SÖS_V68	VHS Fuji super HG	6	
SVT Vuxendöv	V78_	ampex magnetic tape	6	
Tittskåp för Arcreader	MMD461	CD-R80, 700 MB	4	
Nils Bäcklund Alfalaval Samspel inom företag 19750305	LK00826	sound cassette C-60	2	
Arbetlivsinstitutet RA/420719	Ö4HAA_1 1	Dia 35 mm in frame, nr 2 without glass	2	1
Arbetslivsinstitutet Gullätt AB, Bued, Enköping Id8 1973 Dnr 157/ 739	Ö4HAA: 99	35 mm negatives	2	1
Grängesbergsbolaget 'Malm'	SPF431	16 mm, holes just one side		1
	SPF843	Green container, grey reel and film	2	1

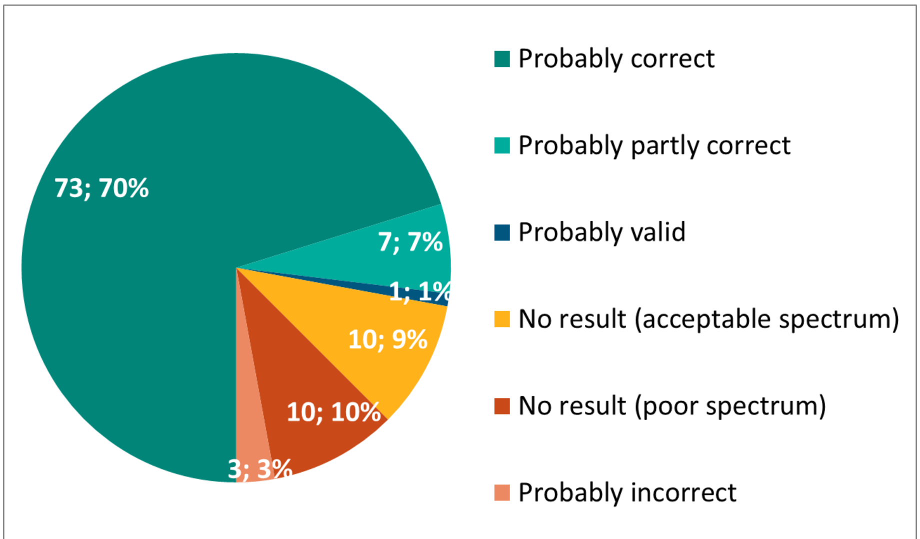

Fig. 20. Categorised results from the SurveNIR "plastics" application measurements at the Swedish National Archives

Categorised results from SurveNIR measurements are shown figure 20 and appendix III. 70% (73 samples) of the results for the materials measured at the National Archives were judged to be probably correct and a further 8% were probably partly correct or valid. These refer, for example, to very thin layers of tapes or transparent parts where the result actually comes from the underlying material, or results where the subtype polymer may not have been identified or is questionable, in particular specifications for PVC-U or PVC-P. As seen before in some objects from the Army Museum the differentiation between plasticised and unplasticised PVC was not always reliable. PVCs vary in their composition with several different plasticisers and other additives being used to influence the materials characteristics. A correct differentiation of PVC-U and PVC-P is important for the decision-making process for preserving actions as plasticized PVC is prone to degradation and needs to be prioritised, while unplasticised PVC is regarded as relatively stable. Here, the SurveNIR results need to be interpreted in combination with other traits of the materials, in particular the materials' flexibility. Looking at the spectral comparison of two transparent map making materials where the results were PVC-U and PVC-P it is difficult to see any significant differences in the spectral peaks and intensity that could explain why they were identified as two different types of PVC, figure 21. However, looking at a comparison between various reference samples of PVC from MoDiP, differences are possible to see in a shoulder at about 6000 cm^{-1} and the peak at about 4600 cm^{-1} for the plasticised PVC, see figure 22.

The ten measurements (9%) with acceptable spectra but no results originated from adhesive tapes and some polyester film references (Secol pockets and PET film from Preservation Equipment limited). The composite tapes (adhesive plus substrate) are not included in the "plastics" application chemometric models but the failure to identify the polyester reference films was surprising. Within the SurveNIR applications filters are set to adjust the result for all spectra together for one category defined as a plastic type. However, the intensity for significant bands in the spectra can differ from sample to sample of a type. According to Dirk Lichtblau, the software and instrument developer, it would be possible to improve the existing filters by increasing the number of samples forming the basis of the chemometric modelling.[9] If no result is obtained but the spectrum is of acceptable quality then the spectrum may be recalculated using "NO FILTERS"; the thus obtained result needs to be assessed by the user regarding plausibility.

The spectra that were of poor quality and therefore yielded no results were obtained from mainly very dark or very reflective surfaces, examples are a VHS cassette, magnetic cassette tapes, a CD record, a LP record and an OH sheet with red writing.
Three measurements (3%) were thought to have given erroneous results; these were a black LP record (result: PTFE) and two dark plastics sheets for map making (results: PC). Polycarbonate would be an unusual material for such sheets and other similar samples were identified as polyester (PET). An overlay of the spectra with a PC reference shows that they are not very similar and the result given by the SurveNIR was very likely false, figure 23.

The results for the eleven samples measured using the "Negatives and Films" application were all judged as probably correct for material type, showing results for cellulose acetate and nitrate. However, there were inconsistencies regarding subtype where different subtypes were shown for the same material. It is important to note that when these spectra were run with the "plastics" application some of the obtained results were false, sometimes showing PVC instead of CN or PVDF instead of CA, see table 6.

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[9] Correspondence with Dirk Lichtblau of Lichtblau e.K.

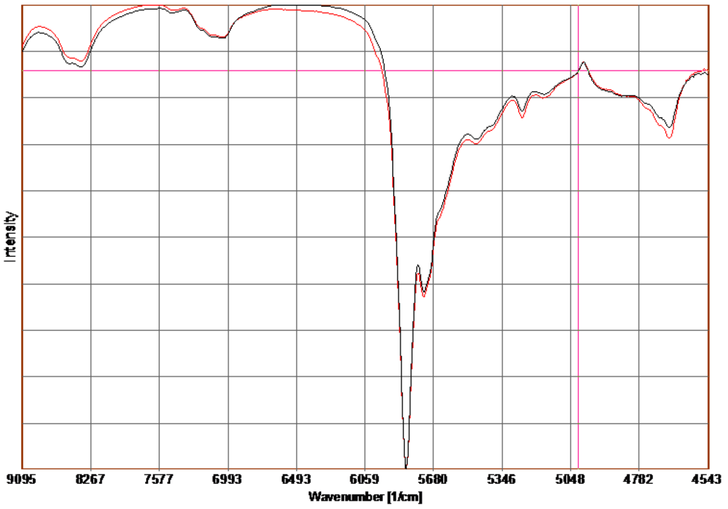

Fig.21. NIR spectra of transparent map making plastic sheets with SurveNIR results: PVC-U (D32) and PVC-P (PlanF).

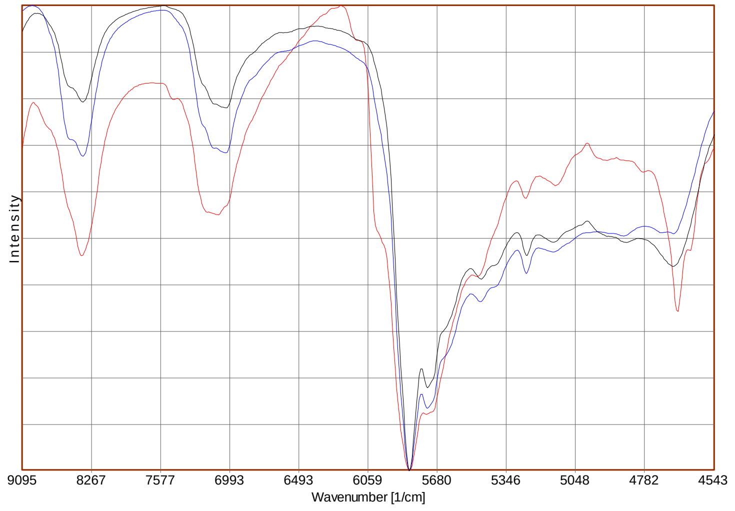

Fig. 22. NIR spectra of MoDiP toolkit samples: PVC-U from sample white rigid, PVC-U from foamed extruded. PVC-P from transparent flexible pipe.

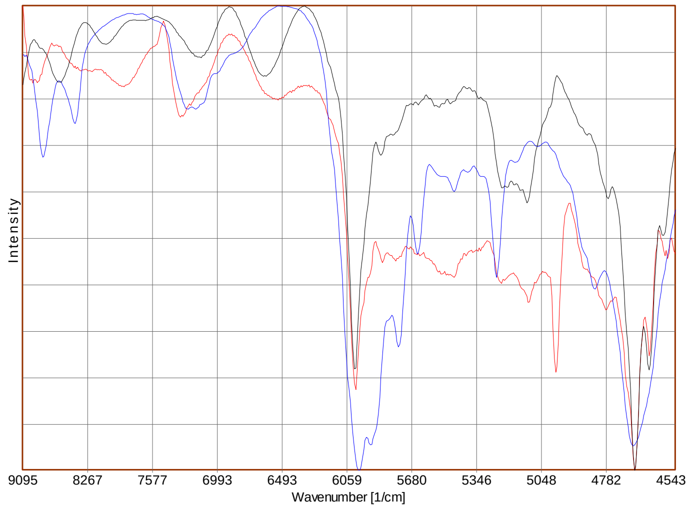

Fig.23. NIR spectra: reference sample PC, map R14 (SurveNIR: PC) and map R13 (SurveNIR: PET).

Table 6. Results of film and negative analyses by SurveNIR for both "Plastics" and "Negatives and Film" applications.

			Plastics app			Negatives and Film app	
Material	**Column 1**	**Comments**	**Group**	**Polymer**	**Suptype**	**Type**	**Subtype**
SMR_K1:2 negative strip 20 p.20	neg	Agfa Isopan F	Cellulose/-ester	CN	-	CN	1
SMR_K12_negp10str2_001	neg	Agfa Isopan F	Halogen Polymer	PVC		CN	1
SMR_K12_negp1str3_002	neg	Kodak Panatomic	Halogen Polymer	PVC		CN	2
SMR_K12_negp1str3_001	neg	Kodak Panatomic	Halogen Polymer	PVC		CN	2
SMR_K21_OECDorig_002_003	film side		No spectra accepted				
SMR_K21_OECDorig_002_002	film part						
SMR_K21_OECDorig_002_001	film part matte						
SMR_K21_OECDorig_001_001	film white matte		Cellulose/-ester	CTA	-	CA	N/A
SMR_K21_OECDcopy_002_001	film part transp grey	Kodak safety film DUP	No spectra accepted				
SMR_K21_OECDcopy_001_001	film white matte	Kodak safety film DUP	Cellulose/-ester	CTA	-	CA	N/A
SMR_K21_film_a_002_002	film brown	Gevaert safety	Cellulose/-ester	CTA	-	CA	1(CTA)
SMR_K21_film_a_002_001	film side	Gevaert safety	Cellulose/-ester	CTA	-	CA	3(CTA)
SMR_K21_film_a_001_002	film white part matte side		Cellulose/-ester	CTA	-	CA	1(CTA)
SMR_K21_film_a_001_001	film white part shiny side		Cellulose/-ester	CTA	-	C	1(CTA)
Film Malm Gränges	on film by no 10	KODAK 19 Safety	Cellulose/-ester	CTA	-	CA	1(CTA)
Film Malm Gränges	shiny side	KODAK 19 Safety	Cellulose/-ester	CTA	-	CA	1(CTA)
Film Malm Gränges	film matte side, 3 cm in	KODAK 19 Safety	Cellulose/-ester	CTA	-	CA	1(CTA)
Ö4HAA_11_003_002	DIA without glass		Cellulose/-ester	CTA	-	CA	1(CTA)
Ö4HAA_11_001_001	Dia with glass, bricka 55		Cellulose/-ester	CTA	-	CA	1(CTA)
Ö4HAA:99_001_003	trough plastic pocket	not possible in pocket	N/A	N/A			
Ö4HAA:99_001_002	neg shiny side edge	Kodak Tri x Pan	Cellulose/-ester	CTA	-	CA	1(CTA)
Ö4HAA:99_001_001	negative exposed part neg 5	Kodak Tri x Pan	Halogen Polymer	PVDF		CA	2(CA)
SJ_SPF1309_002	film outer white layer	acetic smell	Cellulose/-ester	CTA	-	CA	1(CTA)
SPF843_001_003	film light green	acetic smell	Cellulose/-ester	CTA	-	CA	1(CTA)
SPF843_001_002	film light green	acetic smell	Cellulose/-ester	CTA	-	CA	1(CTA)
SPF843_001_001	film light green	acetic smell	Cellulose/-ester	CTA	-	CA	1(CTA)

ATR-FTIR

Four objects were sampled and analysed by ATR-FTIR either to compare with SurveNIR results or when the identification was assessed as an important aspect and the SurveNIR gave a doubtful result, see table 7.

Table 7. Objects from the National Archives analysed by FTIR

Object	FTIR result	SurveNIR result
Degraded and brittle photo corner, Statens maskinprovningar K1:2	regenerated cellulose	Cellulose, but may be the results of the underlying paper material
Container from V78 SVT Vuxendöv	phenylene oxide (PPO). Reported sensitive to both photochemical and chemical deterioration sensitivity.[10]	Blend: PPE+PS
Grängesbergsbolagets film *Malm*	Cellulose acetate substrate with proteinaceous (gelatin?) coating on one side.	CTA
SJ engineering drawing 1MG-15402	cellulose, possibly gummed (indicated by broad carbonyl contribution).	PET (this is likely to be the bulk substrate while the cellulose may derive from a “protective” treatment from ca 1960s using cellulose butyrate or cellulose acetate butyrate, which could also be the cause of the vomit odour of these drawings [11])

4.Conclusions

4.1 Performance of the SurveNIR instrument

The majority of identification results given by the SurveNIR instrument and its “Plastics” and “Negatives and Film” applications are deemed correct, provided the angled window and the correct application is chosen for the materials to be surveyed. The instrument is easy to use, portable and non-invasive. Measurements and results are obtained very fast. As such the overall positive impression of its performance leads to the conclusion that it is useful for investigations of plastic type. Yet, the tests and surveys carried out for this project ascertained some limitations that need be regarded, see section 4.2. In addition, some basic knowledge of plastic materials is required for a confident interpretation of the results.

[10] Grøntoft et al. 2010

[11] Specialist subject Area Architectural Drawings Plastics Historical Society web page

4.2 Limitations of the SurveNIR "Plastics" application

Some important limitations need to be considered when using the SurveNIR for plastics identification. These are limitations resulting from the general NIR technique, the specific SurveNIR instrument and its "Plastics" application, see table 8.

Table 8. Limitations of the SurveNIR for plastics identification.

General limitations of the NIR technique	• Black and very dark objects cannot be analysed as the NIR wavelength range will be absorbed in the material to such an extent that not enough radiation will be reflected back and reach the detector. • Very thin transparent layers on top of another material cannot be analysed as the NIR radiation goes through the thin layer into the underlying material and it will mainly be the absorption in this bulk material that will be analysed. • Very reflecting materials are not possible to analyse as most of the NIR radiation will be reflected back and over saturate the detector leading to a poor quality spectrum.
Limitations specific to the SurveNIR instrument	• Samples cannot be too small for the analysis area of 4 mm in diameter. • Objects need be of a shape that is possible to fit satisfactorily to the angled window. • Semi-transparent objects need to be of a shape that allows the positioning of a back reflector behind the area being analysed. An additional smaller and flatter back reflector could help to overcome this issue in many cases.
Limitations of the "Plastics" application	• The plastics need to have been included in the initial programming of the software, for instance rubbers and formaldehyde resins are not in the plastic application as of this date. There will be no SurveNIR result for those materials. • Sometimes no result is obtained even for plastics that are included in the chemometric model. If the spectrum is of acceptable quality then it may be recalculated using "NO FILTERS"; the thus obtained result needs to be assessed by the user regarding plausibility. • Some polymer subtype identifications are unreliable, e.g. differentiation between plasticized and unplasticized PVC. • Some polymer subtype identifications are not included, e.g. differentiation between polyurethane types –ether and –ester. • Composite materials cannot be identified, e.g. adhesive tapes, textile reinforced resins as the chemometric model does not provide for mixtures. • There are a few instances where incorrect results are given by the SurveNIR "Plastics" application. Some basic knowledge of polymers and experience of plastic types in collections can help to recognise unlikely or questionable results which can be cross-checked through spectral comparisons in the KustaSpec Light software.

4.3 Limitations for the SurveNIR "Negatives and Film" application

The analysis of materials for film and negatives have been shown to be problematic and in need of further development to improve accuracy of identifications. To this end the reference materials for the model need to be expanded. Furthermore, if states of degradation could be added to the chemometric modelling this would serve as a tool for prioritising within the collections and provide a better basis for decision making for preventive actions.

4.4 Condition surveys at the Swedish Army Museum and the Swedish National Archives

The Army Museum
The condition of most objects included in the surveys at the Army Museum was acceptable or good. The polymer identifications have helped to locate objects for prioritised preventive conservation actions, e.g. the physical separation of cellulose esters from other collection items before the emission of acids from the cellulose esters starts to affect objects in the vicinity.

The National Archives
Degradation and damage of objects surveyed at the Swedish National Archives was observed mainly on OH sheets showing paint loss, architectural drawings with deposits and discolouration, negatives deformation and, most prominently, plasticised PVC materials such as pockets, folders, sheets and map making sheets showing tears, stickiness, deformation, yellowing and other signs of degradation, for details see *Assessment of a NIR Spectrometer - Condition of plastic materials at the Swedish National Archives, results from spot-checks*.

An investigation into the degradation processes of the architectural and engineering drawings is needed with a focus on the source of the sour smell and its potential for an acceleration of the degradation processes. Investigations of the degradation patterns and how to best prevent them could be a project to expand in the future. Furthermore, an area for investigation could be how to best preserve the writing on the OH slides or to investigate how the polystyrene butadiene or polyester slide with writing will react with protective folders. As many of the plastic objects found in The Swedish National Archives are of problematic plastics such as plasticised PVC, cellulose nitrate and cellulose acetate the best overall preventive action would be to lower the temperature in storage.

4.5 Making the SurveNIR instrument available to other users in Sweden

The conclusion of the project is that the SurveNIR is useful for identifying plastic if its limitations are understood and taken into account. Plastics are part of many kinds of collections and the SurveNIR could be used by other institutions of cultural heritage in Sweden. The project suggests that a programme for its wider use by other institutions could be set up with the possibility of it being on loan for some time of a year. As one of the Swedish National Heritage Board’s objectives is to facilitate the access of analysis for cultural heritage aims the projects suggests that the loaning arrangements and training in the instrument will be run by the Heritage Board.

Areas regarding the feasibility of such an arrangement that need to be addressed are:
- Agreement with Lichtblau e.K.
- Time periods
- Documentation
- Transport and costs
- Insurance
- Administration
- Other legal considerations

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