Spectroscopic appreciation of RDF and ADF freezing point

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Abstract— **French Civil Aviation Department provides its technical expertise and support for airport and aeronautical matters on the whole French territory. It is involved in the fields of airport infrastructure and equipment, air navigation, environment, air transport safety, and transport security. In the case of winter maintenance, it is specifically in charge of the evaluation of the performance and of the environmental impact appreciations of anti-icing and de-icing materials. A decade ago, STAC started to investigate the benefits of implementing a spectroscopic method in several fields comprising their detection, their identification, their characterization, the monitoring of their biodegradation and the detection of residual amounts. Years of developments have contributed to elaborate a fast, relevant and efficient method to discriminate materials between each other.**

Keywords— ***RDF, ADF, Raman, freezing point***

I. Introduction

Many techniques are implemented to maintain functional systems in winter conditions [1], from ice accretion to freezing of fluid contaminants on airports and on aircrafts. In this latest situation, runways and aircrafts de-icing materials do remain the common tool in airports winter maintenance. These materials are submitted to several regulations and standards, such as SAE AMS ones [2-6]. These materials are mainly applied in a liquid form, once the ice and snow are cleared from the surface and to prevent any new accumulation (Fig. 1). Nevertheless, several concerns are raised with respect to these materials. The first one is obviously their efficiency, i.e. their ability to maintain a freezing point as low as possible, to quickly melt ice or snow, and to remain efficient once diluted. The second aspect is their environmental impact, these chemicals being usually organic compounds (formate, acetate, glycols) [7, 8]. And the last one is their cost, considering the hundreds of tons yearly spread either on ground and aircrafts surfaces [9, 10]. This last concern is strongly related to the two previous one.

Fig. 1 Runway clearing operation (left) and aircraft anti-icing procedure (right).

For years, the behaviour of anti-icing fluids has been the topic of several evolution in SAE AMS standards, which aim is to easily provide a relevant and an efficient information about aircraft de-icing fluids. Muthumani et al. [11] summarized limits of ice penetration ad undercutting tests, as an example. And laboratory instruments, such as DSC, do present the drawback of not being portable and sometimes dependent of experimental condition, such as cooling/heating rate. Over the past five years, a spectroscopic approach has been developed to determine the freezing point of fluids used in transportation infrastructures and vehicles. This method present the main advantage to be able to operate both in a laboratory context than with field constraints [12, 13]. The work presented here will show how this spectroscopic approach is indeed able to provided information about the evolution about the freezing point of de-icing fluids, included once diluted. It will also provide some insights about if implementation in current other characterizations protocols to improve the appreciation of fluids efficiency.

II. Materials, spectroscopic characterization and data analysis

A. *Airports Winter Maintenance Fluids*

Four types of anti-icing fluids are currently used (I to IV), depending on the requested duration of the ice protection of aircraft treated surfaces according to their concentration and the winter precipitation nature (rain, snow, freezing rain) [10]. They mainly are 1, 2-propanediol, with various amounts of thickener, corrosion inhibitors, and also different in colour from each other. Runways and taxiways are usually treated with formate and/or acetate (Table 1). The determination of freezing point was appreciated for pristine products, along with heavily diluted ones, with a large range of dilutions in-between.

TABLE I. General characteristics of some airports fluids

Airport fluid	Composition	Aspect	Commercial name
Type I	1,2-propanediol	Orange	*Safewing MPI 1938* *ECO*
Type II	1,2-propanediol	Yellow	*Safewing MP II FLIGHT*
Type IV	1,2-propanediol	Green	*Safewing MPIV LAUNCH*
Runway fluid	1,3-propanediol and potassium acetate	No color	*Cryotech BX36*

B. *Raman Spectrometer and Fluid Temperature Control*

Raman spectroscopy is implemented for decades in the characterization of materials. It provided information about the chemical bonds present in a material, and as a consequence about its composition. It is an optical non-destructive technique, taking advantage that constraints in the materials can be detected. In the current situation, the phase transition does change way chemical bonds do vibrated, and therefore eases its detection.

Many instruments do exist, with several lasers (532, 785 nm, and other wavelengths), several power outputs (50, 100 mW or over this level, several spectral ranges (175-4000 cm^{-1}, 100-3400 cm^{-1}), and different spectral resolution (4.5, 2 or as low as 1 cm^{-1}), needing integration time as low as a few seconds. Fig. 2 provides illustrations of Raman spectrometers used for fluids characterization.

Fig. 2 Raman spectrometers adapted for RDF and ADF characterizations, with a 4.5 cm^{-1} resolution (left) and a 1 cm^{-1} one (right).

In the case of fluids presented in Table 1, Raman spectrometer consisted in a Kaiser RXN1 operating with a 785 nm laser, with an integration time of 5s, and data collected every 15 s as the fluid temperature changed. Their spectroscopic signatures are illustrated in Fig. 3. No major difference was observed between ADF, but there is a clear distinction with RDF one.

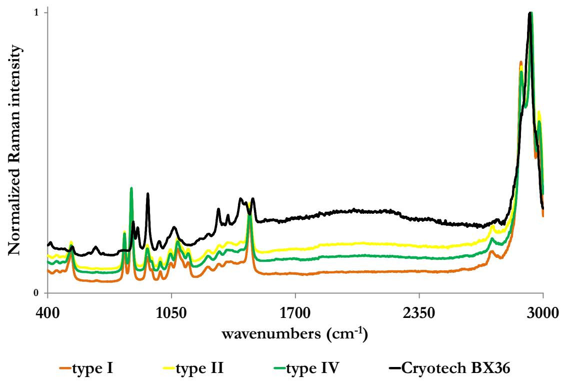

Fig. 3 Raman spectra of fluids presented in Table 1 at room temperature.

Temperature control of fluids can be obtained setting the sample in a climatic chamber, or using a specific thermomicrometer cell from Linkam, as it was the case in this approach. The selected range was -80°C / 0°C. Samples were quickly cooled to -80°C at 20°C/minute. After a 1-minute stabilization at the lowest temperature, the temperature was increased to 0°C at 1°C/minute. The small volume of fluid used in a thermomicrometer cell is a clear advantage since it reduces temperature stabilization durations. It then allows to collecting large amount of Raman spectra to then determine accurately the freezing point temperature. At such a heating rate, and with a 5s-integration time, the sample temperature can be considered as constant at each collected spectrum.

C. Data Analysis Method

The heating rate and the Raman acquisition frequency conducted to nearly 350 Raman spectra. To avoid a long and tedious analysis of each collected spectrum, a specific data analysis was implemented to detect the phase transition from these collected Raman spectra.

This was based on principal components analysis (PCA), to identify a specific structure into the datasets collected for each dilution of each material presented in Table 1. Details on PCA, could be obtained in the literature [14, 15]. This structure will consist in the partition of each dataset into two sub-structures, each corresponding to a phase. It appeared more clearly when treating data without a mean-centered calculation.

III. Freezing Point Determination

Considering the solid to liquid phase transition, PCA applied to collected Raman spectra dataset of each dilution of each fluid will conduct to the emergence of two groups of spectra. Types I, II and IV are all containing 1,2-propanediol, and will mainly differ by the temperature that can be reached before phase transition. The study then focused on types I and IV fluids, and on a RDF. The freezing point is expected to get closer to 0°C as the dilution increases. PCA results are illustrated in Fig. 4.

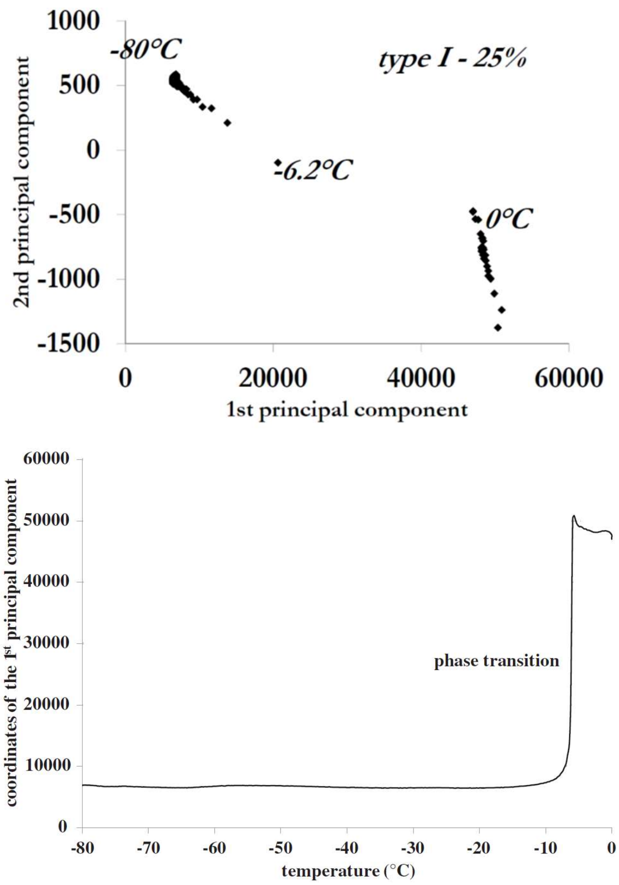

Fig. 4 PCA results in the case of a 25%-type I fluid solution (above), and coordinates of the 1st principal component (below) showing the phase transition.

A partition in the dataset is clearly visible, with an identification of the phase transition. Applying the same methodology to each studied fluid and each generated dilution. Graphs representing the variations of the freezing point as a function of the temperature for all three considered fluids was then elaborated (Fig. 5). Results indicated that the fluids do no longer offer a very low freezing temperature as soon as they are diluted. The dilution does not need to be too large to obtain a freezing temperature close to 0°C.

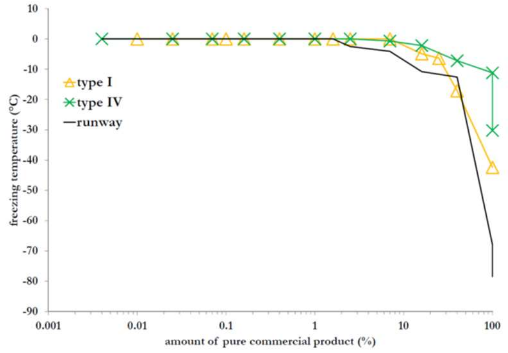

Fig. 5 Evolution of the freezing point as a function of the amount of pure commercial product.

IV. Implementation of a Spectroscopic Approach to Other Fluids Characterizations

As indicated above, RDF and ADF are subjected to several characterizations, starting with the freezing temperature. In the case of these materials, there is a list of specific Aerospace Material Specifications (AMS). In the case of anti-icing performance, a spectroscopic insight will:

- determine the concentration of the fluid when a winter precipitation occurs (Fig. 6),
- determine the incidence of the presence of and ADF mixed with one or more RDF,
- detect the residual presence of a fluid on a treated surface,
- detect the first ice crystals in the case of an ice accretion evaluation,
- contribute to the analysis of biodegradation of organic molecule in an environmental matric (Fig. 7)
- analyse the efficiency of stored products and the ones still present on the ground,
- ...

Fig. 6 Test to determine protective time for an ADF under winter snowfall in a climatic chamber.

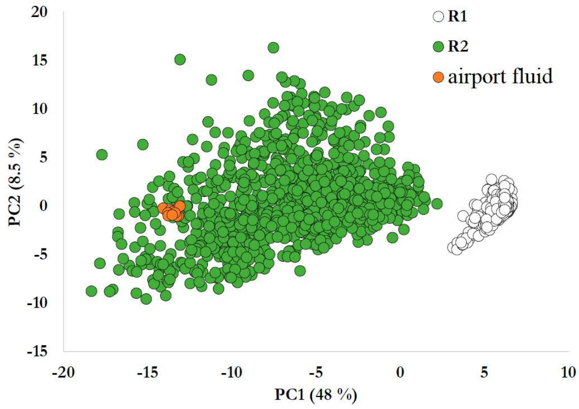

Fig. 7 PCA results of a spectroscopic monitoring of an environmental matrix (R2) contaminated with an airport fluid (orange dots) with respect to the same uncontaminated environmental matrix

V. Conclusions

ADF and RDF are submitted to a large panel of tests to determine their efficiency and their ability to prevent the occurrence of solid phase water on either runways, taxiways and aircrafts surfaces in various winter conditions. Some of these tests do rely on human observation, and on instruments, but they do not offer a full description of the behaviour of the ADF and RDF, in particular with respect to their concentration, their freezing point, or simply their residual presence. Over the past years, Raman spectroscopic was successfully implement, in particular to determine the solid to liquid phase transition, coupled with principal components analysis. It has then clearly demonstrated that the freezing point of ADF and RDF gets quickly close to 0°C as the fluids are diluted.

This spectroscopic approach has already been implemented on the determination of residual RDF amounts and on the identification of the biodegradation process of airports products in an environmental matrix. It could be a relevant complementary investigation tool in some of the many other tests to which ADF and RDF are submitted to, in particular when it comes to detect the fist ice crystals, or to appreciate the protection time of a fluid applied on a surface.

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