Technical Article 1

Addressing the Issues of Significant Figures for Degree of Similarity and Specific FTIR Fingerprint Regions for Paints: A Pilot Study

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Introduction

During a pilot study of Coating Fingerprint certification at a job site and certification training for certified personnel, it was observed that coating inspectors and analysts tend to make two mistakes when reporting the FTIR results. One of the mistakes was about documenting the *r* values in different number of significant figures, while another was about choosing suitable fingerprint regions associated with specific wet paints (*e.g.* 1300-1000 cm^{-1} and 900-700 cm^{-1} for Epoxy part A, 1400-1000 cm^{-1} for Epoxy part B, *etc.*). To solve these, we address the discrepancy of significant figures of *r* values for acceptance or rejection of paint samples (between three and four significant figures) and evaluate a "universal" fingerprint region that can be used for different types of paints by using a statistical test.

Experimental

Three-coat maintenance paints for offshore steel structures – epoxy zinc-rich (coded as EPZ), epoxy (coded as Epoxy) and polyurethane (coded as PU) – were studied. Each paint system, part A and part B, was analyzed using four FTIR different spectrophotometers: Nicolet iS10 (in-house laboratory), Agilent 4300 (on-site screening), Nicolet iS5 (3rd-party laboratory) and Spectrum Two (also as 3rd-party laboratory). All spectrophotometers were equipped with ATR diamond crystal. Three replicate analyses ranging from 4000-700 cm^{-1} at a resolution of 4 cm^{-1} by averaging 32 scans were conducted. For the supplied paints to be accepted on-site, the *r* value must be equal or above 0.900 ± 0.002 [1].

A paired student *t*-test (equation below) was used to compare the difference between (1) three and four significant figures of the *r* values, as well as (2) the choice of fingerprint region (specific vs. universal) for different paints.

$$t = \frac{\bar{D} - \mu_D}{s_D/\sqrt{n}}$$

Null hypothesis ($H_{0(i)}$) assumes that the average difference of studied parameters is zero ($H_{0(i)} = 0$). If the *t*-statistic value is greater than *t*-critical (*t*-critical can be found in the statistic table using the degree of freedom and pre-selected level of significance) and *p*-value that is smaller than 0.05, we reject the null hypothesis.

Results and discussion

1. Number of significant figures for degree of similarity

Different number of significant figures – such as two significant figures, three significant figures and four significant figures – of *r* values have been used interchangeably in the past. Because of this, it confused some certified personnel. The accuracy of measurement for *r* values is then validated by comparing the *r* values between three and four significant figures using the paired student *t*-test. Results (*c.f.* Table 1) for FTIR *high sensitivity compare* function of EPZ part A show smaller values of *t*-statistic as compared to that of *t*-critical and *p*-values that are above 0.05. These indicate that the *r* values with four significant figures are not statistically different than those with three significant figures after round up. Other paint samples (EPZ part B, Epoxy part A and part B, PU part A and part B) follow similar observation (that there is no significant difference between three and four significant figures). For practicality, three significant figures for *r* values are strongly encouraged for the certified coating fingerprint quality controllers to assess the batch-to-batch paint consistency and authentication of paints.

***Table 1**: Paired student t-test to compare the difference between three and four significant figures in EPZ2 sample.*

	$EPZ2_A$_A	$EPZ2_A$_B
$(r_{3sf}-r_{4sf})$	-0.00003	0.00003
s_D	0.00028	0.00031
$SE(\bar{D}) = s_{\bar{D}}/\sqrt{n}$	0.00009	0.00010
n	9	9
$f = n-1$	8	8
t-statistic	-0.359	0.324
| *t*-statistic |	0.359	0.324
t-critical	2.306	2.306
p-value	0.73	0.75

n is the size of $\bar{D}$; *f* is the degree of freedom [defined by (*n* – 1) as it only comprises of the mean of one sample]; *p* represents the level of significance and was defined based on the confidence level from cross-analysis of the *r* values across different FTIR spectrophotometers and different Software. EPZ2 refers to the sample that was given by paint manufacturer 2 (real manufacturer name is not revealed).

2. Specific *vs.* universal FTIR fingerprint regions

Simplification from "specific" FTIR fingerprint regions (1300-1000 cm^{-1} and 900-700 cm^{-1} for Epoxy part A, 1400-1000 cm^{-1} for Epoxy part B, *etc.*) to a "universal" choice of fingerprint region (2000-900 cm^{-1} regardless of the functional groups in different paints) is discussed here. Table 2 shows that all the differences between the *r* values from universal and specific fingerprint regions ($\bar{D}_{\text{universal-specific}}$) are relatively low. The calculated *t*-statistic values of individual paint system are below *t*-critical [*e.g.* 1.000 < 2.306 (*t*-critical) in the case of 2-pack EPZ2 and PU2, and 2.000 < 2.306 (*t*-critical) for 2-pack Epoxy2]. In addition, all the *p*-values from paired student *t*-test are above 0.05. Both fulfilled criteria (*t*-statistic < *t*-critical and $p > 0.05$) mean that the null hypothesis H_0 shall be accepted, that there is no significant difference between the *r* values extracted from "specific" and "universal" fingerprint regions.

***Table 2**: Paired student t-test to compare the difference between specific and universal FTIR fingerprint regions.*

	$EPZ2_{A}\_A$	$Epoxy2_{A}\_A$	$PU2_{A}\_A$
$\bar{D}_{\text{universal-specific}}$	-0.001	-0.002	0.001
S_D	0.004	0.004	0.002
$SE(\bar{D})$	0.001	0.001	0.001
n	9	9	9
f	8	8	8
t-statistic	-1.000	-2.000	1.000
| *t*-statistic |	1.000	2.000	1.000
t-critical	2.306	2.306	2.306
p-value	0.35	0.08	0.35

After accepting the null hypothesis related to the use of three significant figures as well as the choice of universal fingerprint region, the *r* values of EPZ, Epoxy and PU paints were screened at the job site using handheld FTIR and were estimated by *high sensitivity compare* function over the entire (4000-700 cm^{-1}) and universal fingerprint region (2000-900 cm^{-1}).

Figure 1 shows the on-site *r* values of all paint systems that were analyzed using handheld FTIR in reference to in-house generated spectra. For EPZ4 part A, the *r* values generated for the entire FTIR region (4000-700 cm^{-1}) are higher than the threshold limit ($r \geq 0.900 \pm 0.002$) while the *r* values from universal fingerprint region (2000-900 cm^{-1}) is below the threshold. For EPZ4 part B sample, the *r* values generated for the entire region as well as universal fingerprint region are higher than the threshold limit. Similar observations can be seen in Epoxy4 samples. All the samples, including those with the *r* values that are below the threshold limit, were verified further by 3rd-party laboratory.

The result of those that failed as well as passed the screening by handheld FTIR were re-analyzed with benchtop FTIR. The *r* values of EPZ and Epoxy samples from paint manufacturer 4 that had previously failed in the universal fingerprint region (data not shown) during the screening test using handheld FTIR are now above 0.900 ± 0.002. This indicates that the *r* values generated from specific handheld FTIR may lead to a false rejection of the paint samples on-site. The limitation of handheld equipment may be seen in other tools for positive material identification (PMI) such as Raman spectroscopy, optical emission spectroscopy and *X*-ray fluorescence spectroscopy [2].

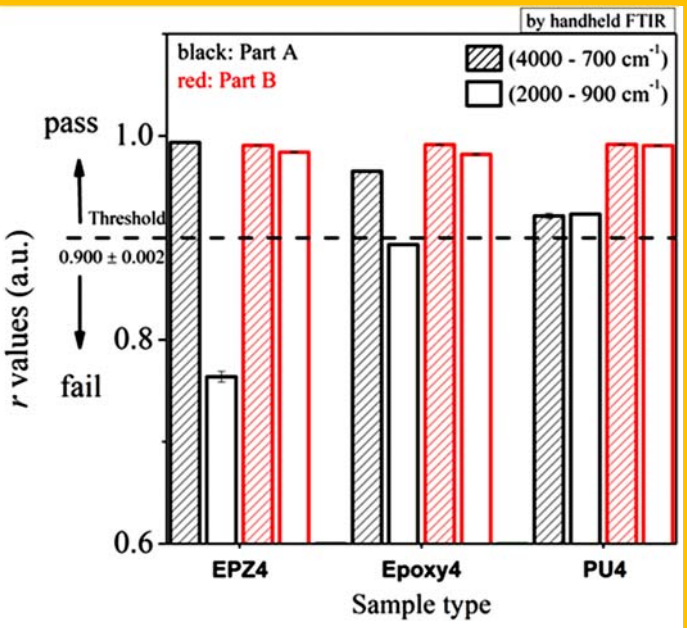

***Figure 1:** Column chart showing the r values of three-coat maintenance paints (from Paint Manufacturer 4) in reference to an in-house generated spectrum. The spectra were obtained using handheld FTIR and analyzed using Software D during on-site screening.*

Conclusion

Based on the outcome of paired student *t*-test, the use of three significant figures for documenting *r* values and the use of universal FTIR fingerprint region were encouraged. Some of the supplied paints may fail during on-site screening when analyzed with handheld FTIR. To avoid false negative results that lead to unnecessary paint rejection on-site, and the affected paint samples shall be re-analyzed using benchtop FTIR in 3rd-party laboratory. In a nutshell, handheld FTIR is only to be used as a screening tool while benchtop FTIR is to be used for verification purposes.

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