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A Top-Down Method for Uncertainty Estimation of the XRFS Outcomes Carried on some up-Conversion Fluorophores

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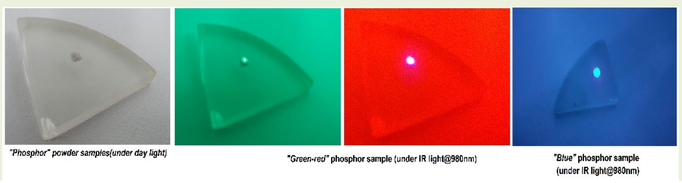
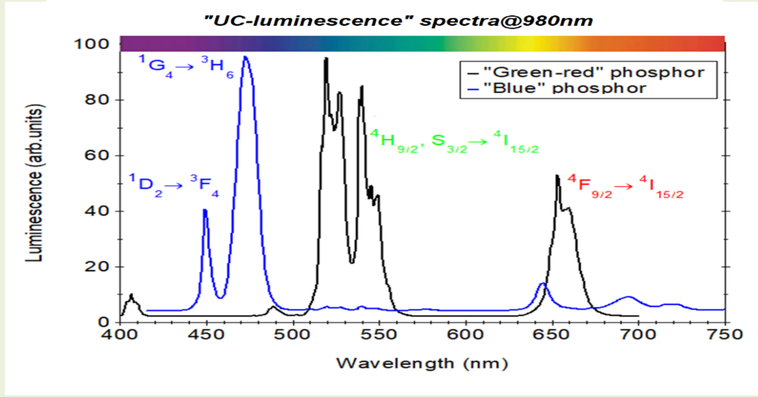
Driving force: The increasing demand for improving the product security has driven an increased interest towards the development of up-conversion fluorophores (UCF) [2]. The ensuring a high quality of a UCF spectral taggant imposes exact composition measurement of UCF. The paper substantiates a new robust top-down method for measurement uncertainty (MU) estimation of the XRFS outcomes carried on UCF. The SEM-EDS data were used to validate this top-down method.

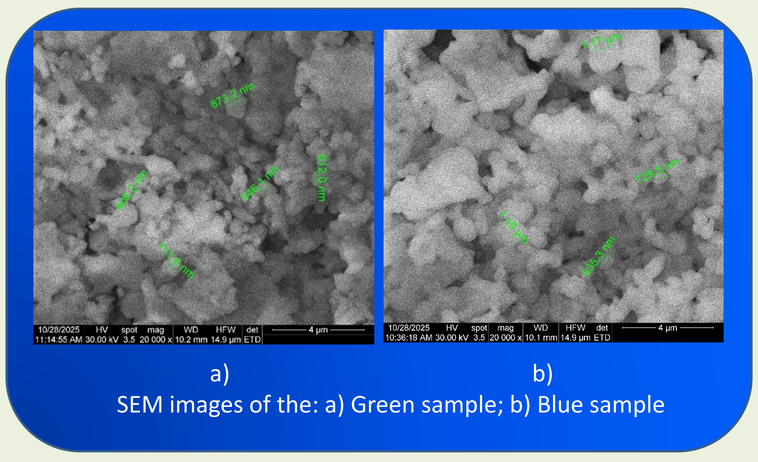
Experimental: Two NaYF4 samples codoped with Yb and Er at different ratios were synthesis through a sol-gel procedure [3]. The measurements were carried with a SciAps X-200 spectrometer and a Zeiss Gemini 500 equipped with an EDS accessory from Bruker.

The sol-gel synthetized UCFs are of globular quasy micronic shape (Fig. 1a,b) and provide mainly green and blue fluorescence under IR 980nm irradiation (Fig. 2.a,b). Hence, they are denoted green and blue samples.



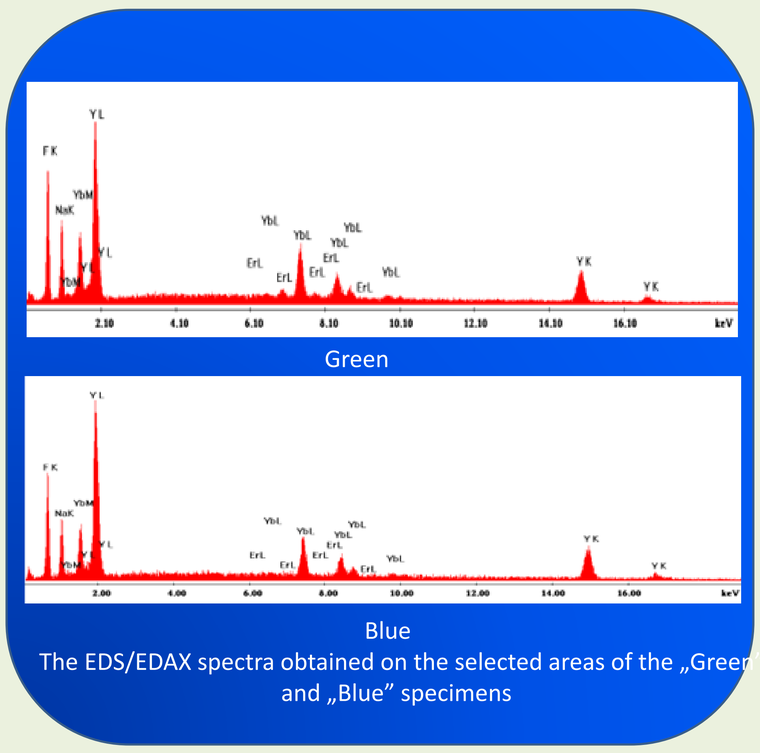


The „Green” and „Blue” UCF specimens (upper side) and their spectra (lower side)



a) b)

SEM images of the: a) Green sample; b) Blue sample



The EDS/EDAX spectra obtained on the selected areas of the „Green” and „Blue” specimens

Element	F	Na	Y	Yb	Er
CGreen(%wt.)	23.62	9.68	43.56	20.25	3.05
SDmean(95%) Green(%wt.)	0.35	0.20	0.76	0.24	0.16
CBlue (%wt,)	24.69	9.21	46.75	19.36	-
SDmean(95%) Green(%wt.)	0.91	0.36	0.83	0.37	0.21

The averaged compositions of the „green” and „blue” samples measured by EDS on 4 selected areas

SciAps Material Report

INSTRUMENT		X200-32165		
Sample Code		UCF Green		
ELEMENTS	Z	C*	SD**	Unit
LE Hydrogen-Fluorine	-	23.41	0.78	%
Na Sodium	11	9.58	0.21	%
Mg Magnesium	12	<8	-	ppm
Al Aluminum	13	8.5	2	ppm
Si Silicon	14	<6	-	ppm
PPhosphorus	15	8.05	2	ppm
SSulfur	16	7.21	3	ppm
K Potassium	19	<6	-	ppm
Ca Calcium	20	10.32	2	ppm
V Vanadium	23	<6	-	ppm
Cr Chromium	24	<5	-	ppm
Mn Manganese	25	<5	-	ppm
Fe Iron	26	<5	-	ppm
Ni Nickel	28	<4	-	ppm
Cu Copper	29	<4	±	ppm
Sr Strontium	38	5.1	2	ppm
Y Ytrium	39	44.11	0.21	%
Zr Zirconium	40	<2	-	ppm
Nb Niobium	41	<2	-	ppm
M Molybdenum	42	<5	-	ppm
Ag Silver	47	<5	-	ppm
Ce Cerium	58	<6	-	ppm
Nd Neodymium	60	<6	-	ppm
Er Erbium	68	2.89	0.13	%
Tm Thulium	69	<6	-	ppm
Yb Ytterbium	70	20.02	-	%
Hg Mercury	80	<5	-	ppm
Pb Lead	82	<5	-	ppm

Meas no. / Element	1	2	3	4	5	6	7	8	9	10	Mean	SD	Median	MEDe (X)
F	23.41	23.52	23.86	23.78	23.52	23.19	23.62	24.16	23.65	23.51	23.62	0.27	23.57	0.18
Na	9.58	9.80	9.71	9.87	9.82	9.69	9.49	9.70	9.59	9.56	9.68	0.12	9.70	0.16
Er	2.89	2.93	2.99	3.04	3.05	3.06	3.08	3.14	3.14	3.16	3.05	0.09	3.06	0.11
Yb	20.02	20.30	20.15	20.11	20.36	20.02	20.25	20.34	20.43	20.55	20.25	0.18	20.27	0.21
Y	44.11	43.49	43.53	42.75	42.66	43.24	44.10	44.55	43.51	43.71	43.56	0.59	43.52	0.64

XRFS outcomes obtained on “green” sample and their statistics calculated via classical and robust statistics (MEDe-ISO 13528/2023)

Element	1	2	3	4	5	6	7	8	9	10	Mean	SD	Median	MEDe(X)
F	22.31	22.28	22.56	22.95	22.94	22.93	23.07	22.73	22.66	22.19	22.66	0.10	22.70	0.37
Na	8.74	8.55	8.66	8.76	8.96	9.07	9.18	9.37	9.29	9.29	8.98	0.09	9.01	0.40
Yb	18.34	18.50	18.89	19.07	18.96	18.93	18.64	18.20	17.77	17.36	18.47	0.18	18.57	0.54
Y	49.69	48.47	47.77	47.75	46.65	47.47	47.94	47.88	48.81	49.47	48.19	0.29	47.91	0.74

XRFS outcomes obtained on “Blue” sample and their statistics calculated via classical and robust statistics i.e. Mean, SD-standard deviation, Median and robust standard deviation (MEDe-ISO 13528/2023)

Conclusions:

The EDS and XRFS results obtained on green and blue UCF samples are compatible. The expanded uncertainty U(95%) assigned to the XRFS outcomes are significant for the first decimal and could make uncertain even the unit figure of the element concentration. However, more attention must be drawn to the exactness of the XRFS and EDS measurement as to ensure a greater exactness (precision and accuracy) of the results. In this regard, we foreseen that further researches must be carried on.

The compositions of the studied UCFs differs significantly from the stoichiometric one as is shown below:

Element	*F*	*Na*	*Y*	*Yb*	*Er*
$C_{Reference}$	*37.14*	11.23	34.76	15.22	1.63
$C_{Green(\%wt.)}$	*23.62*	*9.68*	*43.56*	*20.25*	*3.05*
$C_{Blue(\%wt.)}$	22.66	9.01	48.19	18.47	-

The difference can be interpreted as meaning that F and Na are lost in the sol-gel process, most likely upon calcination, while Y, Yb and Er increase in concentration. Thus, the exact measurement of the powdered UCF composition trough XRFS provides critical details on their synthesis which otherwise can not be obtained.

References:

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