U.P.B. Sci. Bull., Series B, Vol. 83, Iss. 4, 2021 ISSN 1454-2331

VALIDATION OF THE LOI RESULTS OBTAINED ON PARTICULATE WASTE THROUGH MARGINAL RECOVERY AND XRFS METHODS

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LOI is a cost-effective method for waste characterization. The MRCs for LOI calibration are frequently missing on the market. The paper proposes the Marginal Recovery Method (MRM) and combined LOI and XRFS measurements to overcome this drawback. The LOI measurement on spiked waste specimens have recovery yields ≈98%. XRFS and MRM association for validation of the LOI performances for carbonate, organic matter and humidity measurements into metallurgical extractive wastes is the main novelty addressed in the paper. The usage of a low-cost surrogate with MRM for overcoming the missing of MRCs for LOI calibration is another breakthrough that paper emphasizes.

Keywords: loss-on-ignition (LOI), carbonates, marginal recovery, XRFS, uncertainty

1. Introduction

Calcium carbonate ($CaCO_3$), aka calcite, dolomite ($CaMg(CO_3)_2$) and magnesium calcite ($Ca_{1-y}Mg_yCO_3$) are the most common carbonate minerals in soils and implicitly in extractive wastes (EW) [1-3]. Calcite content affects the way of EW valorization [4]. Accordingly, a simple, accurate and inexpensive method for measuring the calcite carbonate content (CCC) is needed. The standard method for CCC measurement in Romania is given in STAS 7707/3-74 [5]. The method is based on sample treatment with concentrated hydrochloric acid (HCl) followed by the volumetric measurement of the released CO_2 using a volumetric Scheibler device [5]. This method is prone to overestimate CCC in case where the specimen

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contains dolomite, magnesium calcite and other substances that may release CO_2 under HCl treatment. The ASTM D 4373–02 standard [6] prescribes the CCC measurement by treating a 1g dried specimen with HCl in an enclosed reaction cylinder (reactor). This standard method was subjected to automation by digital recording of the CO_2 gas pressure values [7].

On the other hand, researchers frequently avoid dealing with HCl from health and work safety reasons. Accordingly, several methods have been developed to determine CCC: gravimetric; titration; loss-on-ignition (LOI), X-ray diffraction (XRD), X-ray fluorescence spectrometry (XRFS), inductively coupled plasma (ICP) etc., [8-13]. The LOI implementation in any laboratory has to take into account that different minerals have different properties concerning change in weight at different heating temperatures [14, 15]. This fact imposes a calibration of the LOI measurement process for each sample matrix. Also, LOI can be strongly dependent on waste composition, on grain size and on the exposure time at sequential temperatures. If LOI is to be used for CCC measurement, then a preliminary test run with a reference specimen of similar composition as the sample of interest must be performed [13]**.**

Literature study has revealed that during ignition, not only organic matter (OM) and carbonates contributed to LOI, but losses in weight may be caused by the evaporation of OH-groups from the crystals in the mineral particles and from the decomposition of carbonates [3, 14,]. Oxidation of certain minerals can cause an adverse phenomenon i.e., increase in weight. The above shortcomings of the LOI applied for CCC measurement are overcome by LECO method [11]. The higher cost of the LECO equipment makes it inaccessible for many geotechnical and environmental laboratories. Hence, LOI method is many times preferred to LECO. Also, the XRD, ICP, XRFS and other methods based on expensive equipment seem to be inappropriate for CCC measurements. In this regard, the paper addresses studies and experimental performed in order to estimate the LOI accuracy which can be obtained in CCC routine measurements.

The marginal recovery method (aka ***surrogate recovery method***) was adopted to assess the accuracy of the LOI method [16]. The EURACHEM Guide [16] defines ***surrogate*** as ”*the pure compound or element added to the test material, the chemical and physical behavior of which is taken to be representative of the native analyte”, while* **Surrogate Recovery** *consist in ”recovery of a pure compound or element specifically added to the test portion or test material as a spike. (Sometimes called "***marginal recovery***")”.* Because LOI is not a chemical method we prefer to denote the surrogate method adapted to LOI as a *marginal recovery method (MRM)*. In the view of EURACHEM Guide, the *MRM is a* ***rational method of analysis*** *i.e., a method that determines an identifiable chemical(s) or analyte(s) for which there may be several equivalent methods of analysis available* [16]. In this frame, the results of the LOI method were validated through comparative tests performed with

XRFS on parallel unspiked and spiked specimens. The results presented in this paper demonstrate that the LOI calibrated by MRM, provides results having sufficient accuracy and, at the same time, it is simple and safe. Also, the LOI calibration through MRM can be performed as routine procedure in geotechnical and waste characterization laboratories. Because certified reference materials (CRM) for CC measurement by LOI are not always commercially available, the MRM is devoted to overcome this shortage. Also, it worth noting that the LOI calibration through MRM can be applied in other important fields e.g., to assess the CCC into ores, or in a metallurgical slag dump etc.

2. Materials and Methods

The LOI measurement have been carried on EW from a Romanian closed landfill. Some samples were spiked with commercial $CaCO_3$ at 10% and 20%, (wt.) levels. Parallel samples were tested by XRFS. The MRM method aims to control the exactness of LOI and XRFS results and to overcome the adequate CRM missing for LOI test.

LOI method is based on sequential heating of the samples in a muffle furnace [3, 15]. The LOI test consists of specimen drying at 105 °C for 6 h in a thermostatic electric oven. Subsequently, the crucible carrying dried specimens were heated at 550 °C for 4h in a Caloris muffle furnace with a ±1 ^{o}C thermostatic temperature control for OM volatilization. Finally, the crucibles were calcinated at 950 °C for 3 h for CCC measurement (Fig. 1). An electronic balance, KERN ABJ 220-4M type, with a $2*10^{-4}$ g accuracy was used for specimens weighing before and after heating.

The water content of the specimen i.e. humidity (H), is calculated as:

$$H = \frac{m_{fC} - m_{105}}{m_S} * 100 \qquad (\%wt) \qquad (1)$$

where m_{fC} is the mass of the crucible filled with raw substance; m_{105} is the mass of the substance and crucible after dried at 105 ^{o}C; m_S is the mass of the raw substance (waste, surrogate) poured into crucible (all in g).

The m_S is calculated as:

$$m_s = m_{fC} - m_C \qquad (2)$$

where m_C is the mass of the dried crucible (g).

OM content of the specimen is calculated as:

$$OM = \frac{m_{105} - m_{550}}{m_S} * 100 \qquad (\%wt) \qquad (3)$$

where m_{550} is the mass of the waste filled crucible after heating at 550 ^{o}C, (g).

Calcium carbonate releases carbon dioxide upon heating, called a thermal decomposition reaction, or calcination (to above 840 °C in the case of $CaCO_3$), to form calcium oxide, commonly called quicklime, according to the reaction:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2\ (\mathrm{g}) \tag{4}$$

where s stands for solid state and g for gas state.

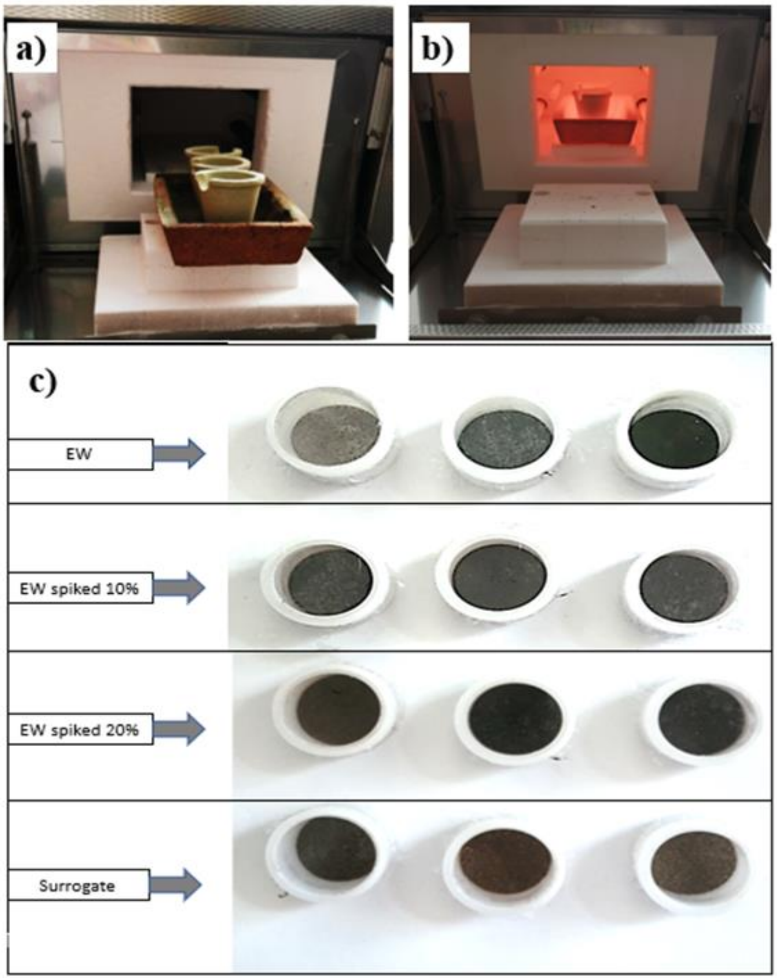

Fig. 1. Details on LOI and XRFS testing: a) heating at 550 °C; b) heating at 950 °C; c) specimens subjected to XRFS analyses.

LOI can be considered as a “blind” method because the weight loss is assigned only to the $CaCO_3$, without any evidence that tested specimen does not contain dolomite or other compounds that release CO_2 during calcination stage. Therefore, LOI provides the CO_2 content, denoted as CCO_2. The CCO_2 at 950 °C is calculated as:

$$CCO_2 = \frac{m_{550} - m_{950}}{m_S} * 100 \qquad (\%\text{wt}) \tag{5}$$

where m_{950} is the mass of the crucible containing waste calcinated at 950°C.

According to Eq. (5) and assuming a molar mass of 44 g/mol for carbon dioxide and a 100 g/mol for carbonate ($CaCO_3$), the weight loss by thermal decomposition at 950 °C multiplied by 2.27 can be considered as the equivalent mass of the carbonate in the original sample, denoted ECC. Hence, the ECC (as a percentage) can be expressed as:

$$ECC = 2.27 * CCO_2 \tag{6}$$

The marginal recovery yields were calculated assuming that the CCC into sample and into surrogate are the mean values obtained by LOI method. The theoretical ECC (g) into a spiked specimen, denoted m_{TC}, was calculated as:

$$m_{TC} = m_W * c_W + m_S * c_S \tag{7}$$

where m_w is the mass of the waste, c_W is the ECC into waste (% wt), m_S is the surrogate mass (g), c_S is the carbonate concentration into surrogate specimen (% wt).

The theoretical concentration of the carbonate into a spiked specimen is calculated as:

$$C_{TC} = \frac{m_{TC}}{(m_{WL} + m_S)} \tag{8}$$

The recovery is defined as [17]:

$$R = \frac{c_{obs}}{c_{ref}} \tag{9}$$

where c_{obs} is the observed concentration (or amount) obtained by the application of an analytical procedure to a material containing analyte at a reference level c_{ref}. The reference level c_{ref} can be provided by [17]:

(a) a reference material certified value,
(b) an alternative definitive method,
(c) a spike addition.

In this case, the reference values are provided on the above b) and c) routes.

In a perfect separation R would be exactly unity. In reality, circumstances such as imperfect extraction often give observations that differ from the ideal. It is therefore a good practice in validating an analytical method to estimate a recovery R for the analytical system. In such experiments, the recovery can be tested for significant departure from unity [17] i.e.

$$\frac{|R-1|}{u_R} \le t \tag{10}$$

where u_R is the standard uncertainty assigned to R, t is a critical value based on t test, t(α/2, n–1), being the relevant value of Student’s t for a level of confidence 1 – α.

If Eq. (10) is true, then R is not significantly different from 1. Else, it is significantly different from 1 and a correction for R must be applied.

According to [17], the factors of the uncertainty budget in recovery estimation that can be considered are:

a) repeatability of the recovery experiment;
b) uncertainties in reference material values;
c) uncertainties in added spike quantity;
d) poor representation of native analyte by the added spike;
e) poor or restricted match between experimental matrix and the full range of sample matrices encountered;
f) effect of analyte/spike level on recovery and imperfect match of spike or reference material analyte level and analyte level in samples.

The factors of the uncertainty budget considered in the paper are:

i) the reproducibility of the recovery experiments;
ii) the repeatability of the weighing and
iii) the calibration uncertainty of the KERN ABJ 220-4M balance.

The error propagation law was used to calculate the uncertainty assigned to the ECC, H and OM [18].

XRFS was considered as the most adequate alternative method to LOI for ECC assaying, as it can identify the Ca elemental content of the specimen and it needs simple specimen preparation [19]. An energy dispersive XEPOS spectrometer with 3D X-ray irradiation geometry, Spectro-AMETEK, was used to measure the elemental composition of the specimens. Based on XRFS outputs it is possible to estimate the phase composition of the specimens, assuming specific oxidation states of the analytes.

The marginal recovery method was applied to overcome the missing of the proper CRMs for the wastes under the study. According to EURACHEM requirements [16], the surrogate should be a pure compound, but pure calcite is expensive, and its purity is beyond the purposes of this study. Hence, the best surrogate for the LOI applied in a testing laboratory was considered a commercial $CaCO_3$ grade. This grade was used, since its elemental and phase compositions can be proper assayed by XRFS measurements. The $CaCO_3$ surrogate was added at 10% and 20% wt., concentration levels in the bulk samples of *circa* 200 g. Specimens from each spiked waste batch were sampled by coning and quartering procedure [20]. Each spiked specimen was homogenized using a Retsch mill, MM301 type, with zirconia balls. The sampled specimens were measured by LOI and XRFS and their outcomes were cross compared. Also, LOI and XRFS measurements were performed on as sampled EW and on surrogate ones.

3. Results and Discussion

Twelve crucibles had been dried until constant mass, weighed and, subsequently, filled with powdered specimens. The 12 crucibles were subjected to the LOI procedure as it is described above and depicted in Fig. 1. a, b. For each specimen under study were used 3 crucibles that were heated simultaneously i.e., parallel test, as to estimate the precision of the LOI through the standard deviation of the mean. The weighing has been performed 3 times in repeatable conditions for each specimen as to assess the weighing uncertainty for each measurand (H, OM, ECC). The average masses of the specimens and the standard deviations (SDs) of their weighing are shown in Table 1.

Table 1.

The average masses of the specimens and the standard deviations (SDs) of their weighing

Specimen type	C*	SD_{C*}	M	SD_M	P	SD_P	N	SD_N	Q	SD_Q
	[g]	[10^{-4} g]	[g]	[10^{-4} g]	[g]	[10^{-4} g]	[g]	[10^{-4} g]	[g]	[10^{-4} g]
EW	21.330	4	32.454	3	32.391	2	32.330	1	32.120	2
	20.672	3	31.432	5	31.332	6	31.251	7	31.044	8
	20.486	3	31.564	4	31.484	3	31.421	2	31.210	3
EW spiked 10%	21.283	4	32.352	4	32.301	3	32.233	4	31.649	5
	21.241	5	32.285	5	32.211	4	32.167	5	31.570	4
	22.333	3	33.262	3	33.201	2	33.145	1	32.573	3
EW spiked 20%	22.346	4	33.169	4	33.074	5	33.008	6	32.060	5
	21.751	2	32.658	4	32,615	5	32.543	4	31.591	3
	20.334	3	31.030	3	30.953	2	30.900	3	29.977	2
Suroggate	21.978	5	32.171	3	32.122	4	32.105	3	28.400	4
	22.028	3	32.338	4	32.288	3	32.268	2	28.521	1
	21.768	5	32.179	4	32.132	5	32.114	4	28.332	3

Note: C-cruciable, M- cruciable+sample, P- cruciable +sample at 105^0C, N- cruciable +sample at 550^0C, Q- cruciable +sample at 950^0C, SD -standard deviation*

The values of the humidity (H), organic mass (OM) and equivalent carbonate (ECC) contents (% wt.), obtained for each specimen under study, and their weighing standard uncertainties are given in Table 2.

Table 2.

The H, OM and CCC values measured by LOI and their assigned weighing uncertainties

Specimen type	H	uH	OM	uOM	ECC	uECC
	[%]	[%]	[%]	[%]	[%]	[%]
EW	0.571	0.004	0.546	0.003	5.10	0.0004
	0.923	0.007	0.754	0.009	5.21	0.0011

	0.724	0.005	0.563	0.004	5.16	0.0006
EW spiked 10%	0.462	0.005	0.615	0.005	14.24	0.0009
	0.671	0.006	0.438	0.006	14.49	0.0010
	0.554	0.004	0.517	0.003	14.13	0.0005
EW spiked 20%	0.879	0.006	0.616	0.007	23.639	0.0011
	0.396	0.006	0.660	0.006	23.567	0.0009
	0.720	0.004	0.497	0.004	23.466	0.0006
Suroggate	0.480	0.005	0.170	0.005	98.139	0.0010
	0.490	0.005	0.188	0.004	98.122	0.0007
	0.448	0.006	0.176	0.006	98.082	0.0011

The weighing uncertainties in Table 2 are of 10^{-4} order, while the variability of any measurands is at least 10 times greater than weighing uncertainty. Thus, the weighing uncertainty is negligible compared to the sub-sampling uncertainty which can be estimated as the standard deviation of the results obtained in 3 parallel tests. This finding is in line with Theory Of Sampling (TOS) which stipulates that sampling uncertainty is the key problem when characterizing particulate wastes [21, 22]. The average values of the H, OM and ECC measurands of the as sampled EW, spiked EW and surrogate specimens are posted in Table 3. Also, the total uncertainty (sampling and analysis) are estimated for each measurand value and are shown in Table 3.

Table 3

The H, OM and ECC results of the LOI measurements

Specimen type	H	uH	OM	uOM	ECC	uECC
	[%]	[%]	[%]	[%]	[%]	[%]
EW	0.74	0.18	0.62	0.12	5.16	0.06
EW spiked 10%	0.56	0.10	0.52	0.09	14.28	0.18
EW spiked 20%	0.66	0.25	0.59	0.08	23.56	0.09
Surrogate	0.47	0.02	0.18	0.01	98.11	0.03

The values of the theoretical concentrations (c_M), measured concentrations (c_T), recovery yields (R) and their associated uncertainties are shown in Table 4. Also, the t factors are calculated according to [17] (Table 4).

Table 4

Comparative data analyses of the MRM outputs

c_S	C_{MC}	C_{TC}	η_C	uCMC	uCTC	uR	t	t(0.025;4)
(% wt)	(% wt)	(% wt)	(% wt)	(% wt)	(% wt)	(% wt)		
Spiked 10%	14.28	14.45	98.84	0.18	0.16	0.017	0.68	3.74
Spiked 20%	23.56	23.75	99.20	0.09	0.08	0.005	1.62	3.74

The data in Table 4 proves that MRM works properly and shows that the LOI accuracy for CCC measurement is approximately 1.2% in case of 10% spiked surrogate and 0.8% in case of 20% one. The LOI accuracy for H and OM measurements is difficult to estimate as they have smaller values that seem close to the limit of quantification. The XRFS analyses provides elemental concentrations of the specimens, based on the integral intensities assigned to the elements as is depicted in Fig. 2.

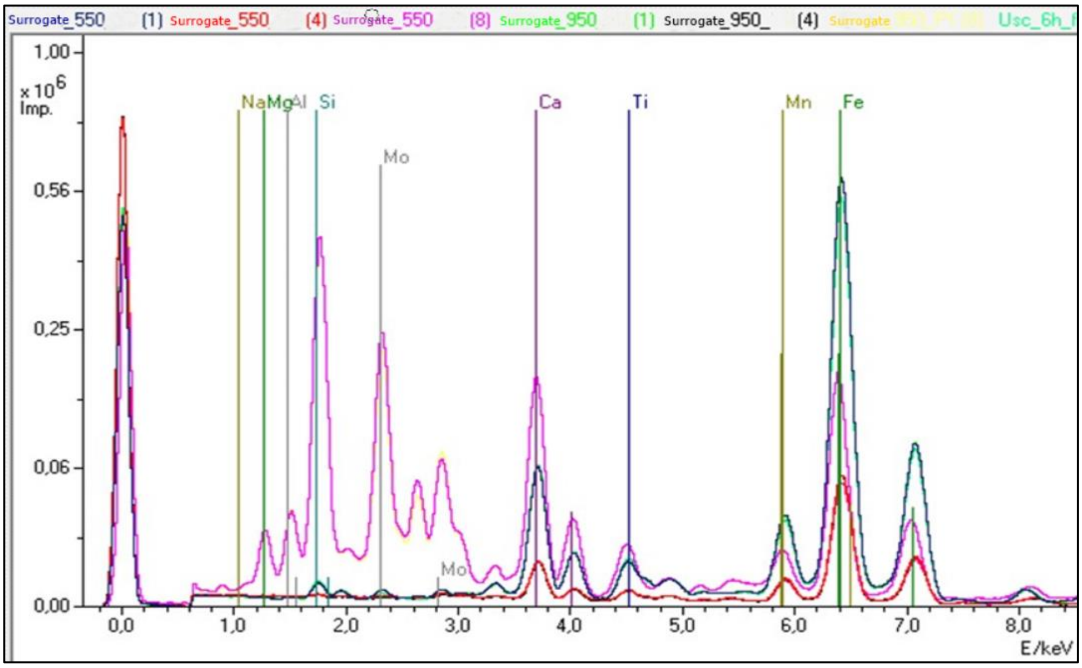

Fig. 2. X-ray spectrum provided by Xepos instrument for surrogate specimen

As could be seem in Fig. 2, the surrogate is contaminated with Na, Ti, Fe etc., but the most probable the elements into specimen are oxidized. Therefore, we used the Xepos facility to provide the oxide composition of the specimen (Table 5).

Table 5

The XRFS outcomes of the investigated specimens and the theoretical ones

	XRFS Outcomes				Theoretical values	
Phase	$CaCO_3$	EW	Spiked_10%	Spiked_20%	Spiked_10%	Spiked_20%
Na_2O	0.21	1.4	1.31	1.22	1.28	1.16
MgO	0.21	2.6	2.29	2.12	2.36	2.12
Al_2O_3	0.12	14.1	12.62	11.20	12.70	11.30
SiO_2	0.25	57.3	51.62	45.93	51.60	45.89
P_2O_5	0.12	0.03	0.04	0.14	0.04	0.05
SO_3	0.14	0.38	0.25	0.42	0.36	0.33
Cl	0.03	0.03	0.02	0.08	0.03	0.03

K_2O	0.23	1.26	1.15	0.97	1.16	1.05
$CaCO_3$	98.47	5.22	14.50	23.78	14.55	23.87
TiO_2	0.15	1.17	1.05	0.87	1.07	0.97
Fe_2O_3	0.06	16.37	14.78	13.04	14.74	13.11
Sum	99.99	99.86	99.64	99.76	99.87	99.89

The data given in Table 6 shows that XRF provides results close to those of LOI.

Table 6

Calcium carbonate ($CaCO_3$) contents (% wt.) measured by LOI and XRFS

Specimen/ Methods	Surrogate	EW	10% spiked EW	20%spiked EW
LOI	98.11	5.16	14.28	23.56
u_{LOI}	0.08	0.06	0.18	0.09
XRFS	98.47	5.22	14.5	23.78
u_{XRFS}	0.08	0.05	0.05	0.06
$t=abs(C_{LOI}-C_{XRF})/sqrt(U_{LOI}^2+U_{XRF}^2)$	3.2	0.8	1.2	2.0

Considering t(0.025;4)=3.747, then the LOI and XRFS results are equal from the Student test point of view. Accordingly, the combined MRM and XRFS provides undoubtful data that LOI provide reliable results with a maximum relative expanded uncertainty of 3%, which is tolerable at least for metallurgical extractive landfilled wastes.

4. Conclusions

This study introduces LOI as a useful method for the measurement of three important characteristics of the metallurgical tailings as humidity, organic mass and mostly calcite content.

The paper proposes marginal recovery as an effective method for assurance the results validity. The effectiveness of the marginal recovery method was checked by XRFS measurements carried on parallel specimens. The inter-comparison of the LOI and XRFS results was done through bilateral t-test with 0.05 significance which proved that they are equal from the statistical point of view.

The association of the LOI, MRM and XRFS for validation of the LOI accuracy for ECC measurement is a new powerful approach. Also, the usage of a low-cost surrogate as reference material for overcoming the missing of MRCs is another breakthrough underpinned in the paper. This study demonstrates that the LOI is well implemented and provides reliable results in the UPB-SIM laboratory.

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